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GENERAL INORGANIC CHEMISTRY

BY

CHARLES BASKERVILLE, PH.D.,
PROFESSOR OF CHEMISTRY IN THE COLLEGE
OF THE CITY OF NEW YORK

BOSTON, MASS.
D. C. HEATH & CO., PUBLISHERS
1909

PREFACE

THE value of a text-book depends upon its teachableness. The teachableness of a book or method, however, depends also upon the teacher, his spirit and the conscientious interpretation of the serious but opportune responsibility that he enjoys. What is contained within these pages has been tried with a large number of students in general chemistry through several years. Satisfactory results have been obtained. That is why it is now offered to others.

The author has unhesitatingly used every source of information, and all devices suggested by other teachers which appealed to him, to make the work effective. The material has been so arranged as to accomplish the most in the least time. Much has been omitted, and the temptation to omit more has been resisted with difficulty.

A knowledge of elementary physics has been assumed, but where the border territory of chemical physics has been entered, sufficient of the general principles involved has been recapitulated, but without detail, to present a logical sequence. No effort has been made to get away from the conception of atoms, yet enough of the modern theories of physical chemistry has been presented to show the student the entrancing fields of interest to the specialist and the scientific methods he makes use of therein. A distinct effort has been made to keep theory and fact in proper proportion, yet some very definite statements are made; but it is assumed that the teacher will explain that some of the laws are true only within limits.

Many historical errors handed down through generations of texts have been corrected. Many methods of preparation used by the alchemist and given in texts these days have been omitted. As a rule, only methods which illustrate principles have been given.

Illustrations and lecture experiments, with a few exceptions, have been omitted, for the teacher then has latitude in presenting the subject. Every laboratory is provided with some apparatus and a lantern, or perhaps a projectoscope, which is to be had now at a small cost; and each teacher has devised lecture experiments, or has used Benedict's or Newth's *Lecture Experiments*, or other works.

Students should take notes on the experiments, write them up at home, and submit them with answers to the questions and problems which are appended to each chapter. The two latter do not always deal with the facts and principles developed in that particular chapter. This causes the student to keep in mind a constant review of what has been studied and impresses the application of the principles. Reference and conversion tables, so convenient in the back of a book, are purposely omitted. A copy of Biedermann's *Chemiker-Kalender*, or Olsen's *Annual*, should be available in each laboratory. The student thus learns how to look up necessary data. Knowledge gained by extra labor sticks.

A *Laboratory Manual* by the author and Dr. Robert W. Curtis, of the same department, is used in conjunction with the text. In it further emphasis is placed upon the observation and correlation of facts and the applications of the underlying principles. It is our practice during the latter part of the work to assign chapters for parallel reading in Venable's *Short History of Chemistry*.

Drs. Curtis, Estabrooke, and Prager, and Messrs. Breithut and Whitaker, of this department, have been helpfully suggestive, but thanks are especially due to my private assistant, Mr. W. A. Hamor, who has followed the proof closely and has prepared the index.

CHARLES BASKERVILLE.

COLLEGE OF THE CITY OF NEW YORK,
May 1, 1909.

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GENERAL INORGANIC CHEMISTRY

CHAPTER I

INTRODUCTION

The study of the phenomena of nature and the speculations arising from the facts observed, looking to an orderly and systematic arrangement of the knowledge obtained, is called *science*. It inquires for the sake of knowledge alone. The application of this knowledge for production, protection, or any utilitarian purpose whatever, constitutes an art, hence we have *pure* and *applied science*. The practical applications of science have often been of great service in the advancement of our knowledge of pure science, therefore no antagonism should exist, as the two branches are mutually helpful.

Nature is so vast and comprehensive a subject, that it has become necessary, with our increasing knowledge of its complexities, to divide its study into several branches. For example, when we study bodies as they are presented to us, at rest or in motion, we call the subject *physics*. When, however, changes occur in the composition of those bodies, through any agency whatever, we call it *chemistry*. In inanimate nature rocks crumble to dust through physical and chemical changes, and we have *geology*. Reaching into space gives us *astronomy*, the physics and chemistry of celestial bodies. When life forces become involved, we have *biology*, and so on. This is more or less an artificial and arbitrary, but a distinctly convenient, subdivision.

Even these branches are subdivided. Chemistry may be *descriptive*, *analytical*, *physiological*, and so forth.

Chemistry may be defined as the study of matter and the changes produced in it by the action of chemical force, or other forms of energy, upon it. As it is primarily an experimental science, we may begin its study by means of experiments.

EXPERIMENT I. If we heat a platinum wire in the air, we observe that it gets red-, or even white-hot. On removing it from the flame it cools, and we have the wire in its original form. We may heat it sufficiently hot to melt it, or even convert it into a vapor, but we have made no change *in* the platinum. It is the same material with which we started, although we may have changed it into the three physical states—solid, liquid, and gas. These are physical changes.* If we weigh the platinum before and after heating, we find it has neither gained nor lost in weight.

EXPERIMENT II. If we heat a magnesium wire in the air, we observe that it burns with a brilliant light and is converted into a white powder, in no way resembling the original material. An actual change in the physical properties of the metal has occurred. In this instance it has been initiated by heat and has continued with the produc-

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* From his knowledge of physics, the reader is supposed to know what is understood by such terms as *matter*, *molecule*, *physical states*, *fusion*, *melting-point* (m.-p.), *evaporation*, *boiling-point* (b.-p.), *distillation*, *distillate*, *sublimation*, *calories*, *latent* and *specific heat*, *specific gravity*, *the laws of the conservation of matter and energy*.

If the assumption is unwarranted, the reader should at once review his physics and postpone the study of chemistry until he has acquired a proper foundation, for we must of necessity describe the materials which enter into chemical transformations and the products obtained by their physical attributes.

tion of heat and light. If we weigh the white powder, we find its weight is greater than that of the original magnesium wire. By this chemical change the magnesium has added something to itself, which must have come from the air. The powder weighs two thirds more; that is, the ratio between the magnesium wire (whatever amount is taken) and the white powder is 3 : 5.

EXPERIMENT III. If we place some red oxide of mercury in a hard-glass test-tube and heat it, we observe a change of color. As the heat increases, and as long as it is applied or until all the red material disappears from the bottom of the tube, we note a vapor given off which condenses as a brilliant metallic mirror on the cooler walls of the tube. If we invert the tube over a piece of paper and tap it, we collect lustrous globules of quicksilver, very different from the red powder we heated. If, before heating, we had lighted a splinter of wood, blown out the flame after a good red coal had formed, and inserted it into the tube before heating, we should have observed that the coal gradually ceased to glow, as it does in the air. In other words, ordinary air was above the powder in the tube. If this is repeated after the heating has begun and when the mirror is forming, the glowing coal bursts into a flame. If we cease heating the tube, the formation of the mirror ceases. This shows the necessity for the continued application of heat. If we again insert a glowing splinter into the tube after all the red powder has disappeared from the bottom of the tube, we note that it no longer bursts into flame. The vapor of quicksilver, therefore, cannot be the substance which makes the splinter burn. If we weigh the tube and red oxide at the beginning and at the end of the experiment, we learn that something has been driven off. A gas was evidently given off, something like air, being invisible, yet different from the air, as shown by the conduct of the splinter. The loss in weight is exactly $\frac{2}{27}$ of the red body.

Experiment IV. If we place a hard lump of quicklime, a cubic centimeter in size, in a tube and pour 2 cc. of water upon it, we observe that the lump swells up, crumbles down into a fine powder, the water seems to disappear, and the tube gets hot. The characteristic properties of the quicklime and water have given way in their combination. Energy in the form of heat has become evident in the change.

Experiment V. If we examine some brimstone (sulphur), we note among other things that it is yellow and not attracted by a magnet, but it seems to disappear in a liquid called carbon disulphide; that is, it dissolves.* If we examine some iron filings, among other things we observe their metallic appearance. They are attracted by a magnet and are insoluble in carbon disulphide.

If we mix 7 g. of these filings and 4 g. of sulphur intimately by grinding in a mortar, and apply a magnet to a portion of the mixture, the iron is drawn away and the sulphur remains behind. Or, if we put another part of the mixture in a bottle, pour in some carbon disulphide, and shake, the sulphur goes into solution. This may be shown by pouring off the liquid and allowing it to evaporate, when we find the yellow crystals of the sulphur in the vessel into which the liquid was poured. The iron remains behind. We can, in fact, make a perfect separation of the sulphur from the iron by repeatedly washing the iron

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* When a substance seems to disappear in a liquid in this manner, we have a solution. The substance dissolved is called the *solute*. The liquid used to make the solution is the *solvent*. If, on evaporation of the solvent, we recover the unchanged solute, we call it a *simple solution*.

with fresh carbon disulphide. The characteristic physical properties, the individualities of the iron and sulphur, have remained the same. In fact, we are able, using a good magnifying glass, to pick the particles of iron and sulphur out of the mixture with a needle.

If, however, we place a third portion in a test-tube and heat it a few minutes, we observe that a part begins to glow. The glow proceeds throughout the mass, even after we cease heating it. If we allow the mass to cool, we note that it has become black and does not resemble either the iron or sulphur. We are unable to pick particles of either out with a needle when we examine it with the magnifying glass. The mass is uniform in appearance. It is not attracted by the magnet. Carbon disulphide does not dissolve it. The individualities of the iron and sulphur have apparently been lost. A new body, with characteristic properties of its own, has been produced, inaugurated through the agency of heat, but once begun, it proceeds until completed.

Experiment VI. If we evaporate 100 cc. of water containing an acid, as hydrochloric acid, we obtain no residue. If we place a piece of zinc in a similar solution, we note that the metal dissolves. A gas is given off, which need not concern us at present. If we evaporate the solution obtained, we get a white residue which does not resemble the zinc in the least. By tests, of which we shall learn later, the presence of the zinc may be shown. It has not been lost.*

Experiment VII. If we connect two sheets, one of zinc and the other of platinum, about 10 cm. square, to the terminals of a galvanometer and dip them into a beaker

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* When the individuality of the solute is changed in this manner, we call it a *chemical solution*.

containing an acid, we get indications of an electric current. A chemical change occurs. The zinc disappears, but is not lost, for if we evaporate the solution, we get a residue similar to that referred to in the last paragraph.

EXPERIMENT VIII. If we insert two sheets of platinum, about 10 cm. square, into a water solution of copper sulphate, and connect them with the terminals of an electric battery, we observe the formation of a red metallic deposit on one of the terminals and the gradual disappearance of the blue color of the liquid.

From these observed facts we learn: —

First, actual changes in the individuality of a substance may take place, differing from the physical changes. These we call *chemical changes*. This constitutes our first conclusion.

Second, chemical changes may take place with or among any of the three physical states of matter, solid (red oxide), liquid (quicksilver), or gaseous (oxygen gas, which made the glowing splinter burst into flame).

Third, chemical changes may be merely inaugurated or continued by the influence of one of the forms of physical energy, heat or electricity, for example.

Fourth, chemical changes may proceed without the initial or continuous aid of one of the varieties of physical energy, yet these changes appear to be accompanied by evidences of such energy. Therefore, we arrive at a second conclusion; namely, chemical changes are intimately associated with, or attributable to, another form of energy, which we may call *chemical energy* or *chemical affinity*. At one time it was called *chemism*.

Joule demonstrated the *law of the conservation of energy*. If the physical forms of energy, like heat, light, and so forth, are convertible into chemical energy, and *vice versa*, we assume that this constitutes no exception, although frankly we are not able to prove it absolutely. No case of chemical action has ever been observed, and many thousand careful studies have been made, without evidences of other forms of energy. Chemical actions are always accompanied by heat demonstrations (either absorption or evolution),* often by electricity as well, and frequently by light, and even sound. On account of this contamination, as it were, we do not at present know any accurate method of measuring this chemical affinity.

EXPERIMENT IX. If we shake 1 g. of sodium chloride (table salt) crystals in 50 cc. of water, a clear solution is obtained. If we boil off the water, we get back our crystals of salt. If this is done carefully, we lose none of the salt, and apparently there has been no change in that substance. If we dissolve 3 g. of silver nitrate in 50 cc. of water, we get another simple solution. If we pour the two clear solutions together, a white clotty solid is formed at once. This may be separated by filtering.†

If the filtrate is evaporated and carefully dried, a white

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* When heat is given out, the action is *exothermic*. When heat is absorbed, *endothermic*. As a rule, the tendency is in the direction of the evolution of heat.

† When we produce a solid, that is, a substance which is insoluble in the liquid present, by bringing two clear solutions together, we call it a *precipitate*. The substance added to produce the precipitation is the *precipitant*. We may separate the precipitate from the liquid by filtering. The process of *filtration* depends upon passing the liquid, in which the precipitate is suspended, through a porous material which is itself usually not affected by the liquid or solid and which should have pores so small that the solid is held back, yet the liquid passes freely. The liquid, after it has been filtered, is called the *filtrate*. Sometimes the solid passes through also, and the filtrate is turbid. This indicates that the pores are too large or that the precipitate has not been sufficiently agglomerated. To accomplish this requires special treatment, which varies with substances and conditions. Filters are made of unsized paper, cloth, sand, glass-wool, asbestos, and so forth.

crystalline substance is obtained, which we find weighs about 1.5 g. If we moisten a piece of paper with a water solution of this body, dry it, and set it afire, it burns vigorously with a yellow flame. If we do the same with a solution of the original sodium chloride, the paper burns with a yellow flame, but very slowly. If we do the same with a solution of the silver nitrate, the paper burns vigorously, but no yellow flame is obtained. It is reasonable to suppose that there is something in common with the salt and the residue which produced the yellow flame. It is also reasonable to think that there is something in common with the silver nitrate and the residue which causes the paper to burn in a lively manner.

The clotty precipitate, being insoluble* in water, is quite different from the other two substances, and has been produced by their presence in the same liquid. If it is collected by filtration, washed, and dried, we find it weighs about 2.5 g.

The *fifth* fact observed is that the sum of the weights of the new substances produced by the action (precipitate plus residue from evaporated filtrate in this case) is equal to the sum of the weights of the two materials used originally (salt and silver nitrate). Therefore (third conclusion), *chemical energy which produces deep-seated changes in matter, neither creates nor destroys it.* Chemical energy therefore presents no evidence in opposition to the *law of the conservation of matter.* Lavoisier, in 1783, demonstrated this when he performed the third experiment, weighing the red oxide, quicksilver, and oxygen.

If we perform Experiment V. by heating a mixture of 8 g. of iron and 4 g. of sulphur instead of 7 and 4 g. respec-

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* As all substances are more or less soluble in water, when we use the term *insoluble*, we actually mean *extremely slightly soluble.*

tively, we observe some iron is removable from the ground-up mass by the magnet, but not all. No sulphur is removed by carbon disulphide. If a mixture of 7 g. of iron and 5 g. of sulphur is treated similarly, no magnetic properties are noted, but a portion of the sulphur, although not all, is removed by carbon disulphide. We must have the iron and sulphur in the exact proportion of 7 : 4 in making the new body, to avoid having some iron or sulphur left over.

Any excess of either substance involved in a chemical change remains as such unused; this constitutes a *sixth* fact from which we may draw a fourth conclusion; namely, *every substance has a definite composition.* A definite amount of one substance requires a fixed ratio of a second substance to produce a third.

The union of substances is called *synthesis*, and the product obtained a *compound* (Exp. II.). A definite amount of one substance breaks up into a fixed ratio of two or more other substances (Exp. III.). This rupture of a compound is spoken of as *analysis*. When we have exhausted all means at our command for breaking a substance up into other constituents, we say it is a *simple substance.* Compounds are composed of simple substances and always in definite fixed proportions, which facts give us the *law of constancy of composition* or *definite proportions*. We know of no exceptions to this law, and we know the composition of many tens of thousands of compounds.

EXPERIMENT X. If we take two glass cylinders, each of 1 l. capacity, provided with ground tops and glass covers, we may fill them with gases. A description of the procedure is unnecessary, as practice in the manipulation is had in the laboratory. We fill one cylinder with the gas obtained from aqua ammonia. We fill the other with a gas obtained from muriatic acid. We note that both are colorless, fume in the air, and each has its own distinct sharp odor. By applying a little vaseline to the glass covers, the gases may be safely confined within the cylinders. One cylinder is inverted and placed upon the other, so that the glass covers form a partition separating the two gases. By a deft movement this partition may be withdrawn, the mouths of the cylinders fitting snugly, and the gases are brought together. At once a dense white cloud forms, but this soon settles as a white powder upon the walls and bottom of the cylinders. A chemical change has taken place. A solid has been produced when the initial substances were gases.

Because gases expand and contract through wide ranges of volume under the influence of changing pressures and temperatures, we say they are in molecular condition. *Chemical changes take place between molecules* is our fifth conclusion.

This must also be true for those changes which occur in solutions. Our reason for making this statement depends upon a few simple facts. If we remove equal amounts from the top, middle, and bottom of a salt solution, like the one used above (Exp. IX.), we find them equally salty and on analysis that they have the same composition. If the same amount of salt is dissolved in twice, or any number of times, that volume of water, we find the solid uniformly distributed throughout the liquid. In other words, the salt in solution is distributed throughout the volume of the liquid, whatever volume it may occupy. Gases distribute themselves throughout the volume of the containing vessel as molecules, therefore it appears that the solid (or other form of substance) in solution is in a similar condition. *Demonstrations of chemical* *affinity are facilitated by those conditions which give molecules the greatest freedom of motion.*

EXPERIMENT XI. If we repeat Experiment III., using the greenish black oxide instead of the red oxide of quicksilver, we observe first a mirror and at the same time the production of the red form, but no oxygen gas is generated. On continuing the heat, this red form gives the same results as that used in the former experiment; hence it is the same material. If we weigh the tubes in both instances at the beginning and end of the experiments, we note that the ratio of quicksilver in the red oxide to the gas given off is 25 : 2 and with the other oxide 50 : 2.

We see that two different compounds may break up into the same two simple substances, but in different proportions; or the converse, two simple substances may combine in different proportions to form two different compounds. In this case we observe just twice as much quicksilver in one substance as in the other, that is, a multiple. From examination of many thousands of compounds, it has been learned that this is always the case; hence we have our sixth conclusion, namely, the *law of multiple proportions*, that is to say, there must be some minimum amount of each simple substance which enters every compound, either as such or some multiple.

When we endeavor to understand the facts observed and the conclusions drawn, a tentative explanation is first put forward. This is an *hypothesis*. When accumulated facts accord with the hypothesis, it is termed a *theory*.

From the facts obtained from the experiments, we are warranted in reaching the same conclusion arrived at by John Dalton in 1803, although he used different experiments; namely, that chemical action takes place between molecules, and that the molecules are composed of smaller, invisible, indivisible, unchangeable particles which he called *atoms*. An atom is the minimum amount of a simple substance. As matter has weight, — that is, upon our globe it is attracted through the agency of gravity, — the molecules of which matter is composed must have weight. In turn, if the molecules are composed of atoms, the latter must have weight; this we call the *atomic weight*. As many thousands of facts observed during the last century have been in accord with this hypothesis, it has become known as the *atomic theory* and has been of inestimable value in the development of our knowledge of the science of chemistry.

Within the last decade of the nineteenth century, however, experimental evidence has been obtained, which, according to one school of scientific men, has thrown some doubt on the theory as generally accepted. This in brief is as follows. The hydrogen molecule, the lightest known molecule, has been supposed to be made of hydrogen atoms, the lightest atoms known. Thirty years ago Crookes found that an electric current could be passed with great ease through hydrogen gas under extremely small pressures. He suggested the existence of an ultragaseous state of matter, a *protyle*, of which all matter is composed, and that its particle weighs about one thousandth that of a hydrogen atom. J. J. Thomson, following an elaborate procedure, weighed these particles, not singly, of course, but in quantity, and found that the value was between 800 and 1000. As they bear electric charges, he designated them *electrons* (*corpuscles*, according to Lodge).

By definition, an atom means something which cannot be divided. We have been accustomed to apply the term to that chemical particle which has *not yet* been divided. As soon as it is shown to be complex, the particle ceases to be an atom. As language changes, there can be little objection, if it be done by common agreement, so there may be no misunderstanding, to applying the term *electron* to a real atom or the real indivisible particle. Men of science do not hesitate to discard one theory to accept a better one, yet they do not embrace the new simply on account of its novelty. The evidence accumulated at present is scarcely sufficient to warrant the abandonment of the atomic theory, especially when it is used so satisfactorily for the purpose of systematizing chemical science.

EXERCISES *

1. How does a simple solution differ from a chemical solution?

2. What are the grounds for assuming that substances in the gaseous state are in the molecular condition?

3. Suppose two solutions, when brought together, produce a solid. How may we collect this solid, and what principles are involved in that collection?

4. Is the line of argument outlined in this chapter leading to the assumption of the existence of atoms logical? If so, why so? If not, why not? And what other conclusion would you draw, and why?

It is the everlasting duty of science to seek the truth, as far as we are able to conceive it. If the conclusions are

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* The reader is advised to give the closest attention to these exercises. It is urged that he write out a solution of each problem presented. A clear exposition will show his understanding of the facts to which attention is directed and the principles involved. Some exercises are given which serve to refresh what has been previously treated. Students should be required every week, as a part of the home work, to submit notebooks containing a full account, in their own words, of these exercises. If this is done conscientiously, examination time will carry none of its usual bugbears.

not logical, it is not science. True, our logic may appear false at times through our lack of knowledge or the misinterpretation of facts. This latter we should avoid; therefore, the utmost frankness between teacher and student must prevail.

CHAPTER II

THE CHEMICAL ELEMENTS

We know many different kinds of substances. As a molecule is the smallest particle of a substance which exhibits the individuality of the substance, there must be as many different kinds of molecules as there are different kinds of substances. However, we know only about eighty different kinds of atoms. These atoms, singly or combined in twos, threes, or in larger numbers, give us the great variety of substances known. In compound molecules there are two or more different kinds of atoms. In addition to those combinations which we find in nature, numerous other combinations have been brought about in the laboratory, and yearly many are added to the list. Perhaps the possible number of compounds might be determined mathematically, but such a calculation would be a tedious and prolonged labor. This impresses itself when we later learn that thirteen carbon and twenty-eight hydrogen atoms may combine, theoretically, in 802 different ways, giving corresponding compounds. Even a consideration of all known substances would be an uninteresting task; but a study of the systems which have been evolved and the principles underlying these systems is one of great fascination.

This may best be begun by a consideration of the simple substances, those whose molecules contain only one kind of atom. These we call the *elements*. The elements may have only one atom in the molecule or several. It follows that the number of elements must be limited to the number of different kinds of atoms known. We may discover some unknown at present or we may show the complexity of some now thought to be simple, but the actual number of different kinds of elements in the world cannot be added to nor taken from.

In this connection it should be said that a philosophical idea has come forward at intervals ever since man began pondering on these matters; namely, that there is, or was, one, the simplest substance of which all matter is, or was, made. If that be true, — and perhaps it is, — then we only require the knowledge of how to change one element into another and the necessary apparatus to make the idea an accomplished fact. The thought was prominent in the discussions with and even before the early Greek philosophers. It dominated the pre-chemistry period, when the true alchemists, like Geber in the eighth century, and their charlatan camp followers, sought to change silver and the other metals into gold. It prevailed for a long time after Roger Bacon in the thirteenth century said that nature had made the change, but that it had taken ages to accomplish it. The true end, he said, should be the finding or making of the "philosopher's stone," with a pinch of which man could accomplish those changes in a short period. With the final establishment of the law of the conservation of matter by Lavoisier in the last quarter of the eighteenth century, the idea appeared to be doomed from an experimental point of view. Within the past decade a new element, radium (Chap. XXV), has been discovered. Under certain conditions, it changes into another element, helium (Chap. XII). The transmutation of the elements has been experimentally demonstrated. While these statements appear to be contradictory, in fact they are not, when the terms used are clearly understood. By our definition, radium cannot be an element, because its molecule breaks up into something else, yet it has a recognized place in the table of elements. This latter fact is due to an agreement among chemists to recognize a substance as an element which, under proper conditions, exhibits a spectrum showing characteristic lines possessed by no other element and possesses a definite combining weight. Radium satisfies these two requirements and constitutes an exception to the general proposition of the consistency of atoms in an elementary molecule. If we retain the term *element*, and there is no indication of its being discarded soon, its definition must be broadened.

Of the several hundred substances which have been proposed as chemical elements, only about eighty have been agreed upon.* On the next page will be found an alphabetical list of the elements recognized at the present time (1909). Owing to the progress of science this is not fixed and unchangeable, new elements being added from time to time, others being removed when resolved into constituents. Oftentimes, when that occurs, the name of the complex is given to one of its constituents (lanthanum was broken up into lanthanum and didymium). No changes are made, however, without a most thorough scrutiny on the part of many.

No general system has been followed in naming the elements. Some have been known from the earliest times, and their common names have persisted in use. In most cases such names have followed the linguistic changes (iron, copper). Some have been named after some characteristic property they possess (chlorine, bromine), or

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* A complete list of these, with full information, is to be found in "The Chemical Elements" by the author, from the press of John Wiley & Sons, New York.

THE CHEMICAL ELEMENTS

INTERNATIONAL ATOMIC WEIGHTS, 1909

Aluminum	Al	27.1
Antimony (Stibium *)	Sb	120.2
Argon	A	39.9
Arsenic	As	75.0
Barium	Ba	137.37
Beryllium (Glucinum †)	Be *or* Gl	9.1
Bismuth	Bi	208.0
Boron	B	11.0
Bromine	Br	79.92
Cadmium	Cd	112.40
Cæsium	Cs	132.81
Calcium	Ca	40.09
Carbon	C	12.00
Cerium	Ce	140.25
Chlorine	Cl	35.46
Chromium	Cr	52.1
Cobalt	Co	58.97
Columbium (Niobium †)	Cb *or* Nb	93.5
Copper (Cuprum *)	Cu	63.57
Dysprosium	Dy	162.5
Erbium	Er	167.4
Europium	Eu	152.0
Fluorine	F	19.0
Gadolinium	Gd	157.3
Gallium	Ga	69.9
Germanium	Ge	72.5
Gold (Aurum *)	Au	197.2
Helium	He	4.0
Hydrogen	H	1.008
Indium	In	114.8
Iodine	I	126.92
Iridium	Ir	193.1
Iron (Ferrum)*	Fe	55.85
Krypton	Kr	81.8
Lanthanum	La	139.0
Lead (Plumbum)*	Pb	207.1
Lithium	Li	7.00
Lutecium	Lu	174
Magnesium	Mg	24.32
Manganese	Mn	54.93
Mercury (Hydrargyrum *)	Hg	200.0
Molybdenum	Mo	96.0
Neodymium	Nd	144.3
Neon	Ne	20.0
Nickel	Ni	58.68
Nitrogen	N	14.01
Osmium	Os	190.9
Oxygen	O	16.00
Palladium	Pd	106.7
Phosphorus	P	31.0
Platinum	Pt	195.0
Potassium (Kalium *)	K	39.10
Praseodymium	Pr	140.6
Radium	Ra	226.4
Rhodium	Rh	102.9
Rubidium	Rb	85.45
Ruthenium	Ru	101.7
Samarium	Sa	150.4
Scandium	Sc	44.1
Selenium	Se	79.2
Silicon	Si	28.3
Silver (Argentum *)	Ag	107.88
Sodium (Natrium *)	Na	23.00
Strontium	Sr	87.62
Sulphur	S	32.07
Tantalum	Ta	181.0
Tellurium	Te	127.5
Terbium	Tb	159.2
Thallium	Tl	204.0
Thorium	Th	232.42
Thulium	Tm	168.5
Tin (Stannum *)	Sn	119.0
Titanium	T	48.1
Tungsten (Wolframium *)	W	184.0
Uranium	U	238.5
Vanadium	V	51.2
Xenon	Xe	128
Ytterbium (neo-)	Yb	172
Yttrium	Yt	89.0
Zinc	Zn	65.37
Zirconium	Zr	90.6

* Alternate Latin names.

† Alternate names.

compound in which they occur (nitrogen), or the planets (uranium), or some mythological character (thorium, tantalum), or the country of the discoverer (gallium, germanium). The names of many of the so-called metallic elements end in "-ium."

The accepted atomic weight is placed in the third column. In other places we shall learn some of the principles underlying the determination of these figures, but one or two points require explanation here. The figures are not absolute, but relative. For instance, 11 opposite boron does not mean 11 grams, 11 pounds, 11 tons, or any definite weight except in comparison with the other elements. If we have 23 grams, pounds, or tons of a compound whose molecule contains one atom each of boron and carbon, we have present 11 grams, pounds, or tons of boron and 12 of carbon.

As they are relative, we are at liberty to select any unit as a basis. It would be only natural to place the lightest at 1; and this was done for a while, but we find none in our table with that figure. We find for hydrogen 1.008. If hydrogen were placed at 1, then the value for oxygen would be 15.89, whereas it appears as 16. The reason for this is purely utilitarian. The chemists of one nation used hydrogen 1 and oxygen 15.89, while chemists of another nation used hydrogen 1.008 and oxygen 16. There was no uniformity even among the chemists of any one nation. Consequently there was constant confusion in scientific literature and often grave differences in commercial transactions, due to the use of one value here and the other elsewhere. As the value is determined mainly from the compounds, and oxygen forms compounds with more of the different elements, especially the metals, than does hydrogen, it was agreed among the majority of chemists, through accredited representatives, to regard oxygen as the standard and place its value at 16. No figure beyond the second decimal place is used for any element, except hydrogen, whose value in direct comparison with oxygen has been most accurately determined.

In the middle column will be found the *symbols* of each element. They are used not only for abbreviation, as the figure "7" is used instead of the word "seven" in mathematical calculations, but often to indicate an atom or molecule, or a definite relative weight of the element. These symbols are selected by taking the initial letter of the name, the Latin name being used where shown, and writing it as a capital. If there are several with the same initial letter, as carbon, cadmium, calcium, chlorine, cobalt, copper, etc., it is followed by a characteristic small letter in the name, in this manner: C, Cd, Ca, Cl, Co, Cu, etc. It is not necessary to memorize these names, atomic weights, or symbols at once. Their frequent use soon makes one sufficiently familiar with them.

Clarke has calculated the relative abundance of the elements in a sphere comprising the crust of the earth for a depth of ten miles, the ocean, and the atmosphere.

	PER CENT		PER CENT
Oxygen	49.98	Carbon	0.21
Silicon	25.30	Chlorine	0.15
Aluminum	7.26	Bromine	
Iron	5.08	Phosphorus	0.09
Calcium	3.51	Manganese	0.07
Magnesium	2.50	Sulphur	0.04
Sodium	2.28	Barium	0.03
Potassium	2.23	Nitrogen	0.02
Hydrogen	0.94	Chromium	0.01
Titanium	0.30		

There are several variable factors in the table, which prevent its being absolute. The composition of the interior of the earth is not known. All the elements are not included in the list, especially those with the largest atomic weights, hence, although interesting, we may select another method for inaugurating the study of the elements than one founded upon abundance. As the atomic weight is fixed, we may begin either with the lightest or the heaviest. Inasmuch as the lightest element is a constituent, with the most abundant one, in the most plentiful compound and familiar substance, water, we may begin with that.

EXERCISE

Draft a clear explanation of what is meant by a chemical element.

CHAPTER III

HYDROGEN

THE freezing of water, melting of ice, boiling of water, and condensation of steam illustrate the ease with which a familiar substance may be converted from one physical state into another. These changes are regarded by some as chemical, for ice, water, and steam exhibit distinct individualities. The molecules of ice, water, and steam, however, contain the same atoms and in the same proportions, so for our purposes we may regard them as the same.* We may ask them some chemical questions, as it were, by experiments.

EXPERIMENT I. If some iron filings are placed in a tube which is heated red hot, and we pass steam through the tube, we observe that iron rust has been formed; and the excess of steam coming from the exit, after condensation, shows the presence of a colorless gas not present as such in the original steam. This gas is not given off by the iron when heated alone, nor does it produce rust when passed over fresh iron. The iron rust weighs more than the original iron. This shows that a metal may take something away from the steam. The water molecule

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* We do not know the number of atoms in a molecule of water or ice, although we do for steam. This is a good illustration of the close relationship between the several branches of science and the difficulty in drawing a sharp line between physics and chemistry.

must be made up of at least two kinds of atoms, one that causes iron to rust and one that does not. What are they?

EXPERIMENT II. It is more convenient to experiment with liquids, where possible, than with gases on account of the difficulties in handling the latter. In this experiment we shall use water, and a different metal, as iron does not rust in pure water. If we place a piece of red litmus paper * in some water in a beaker or other suitable vessel, we note that it becomes wet. If we throw a piece of sodium on the water, we observe that it melts, spins around, and finally disappears. The water now not only wets the litmus paper but turns it blue. A chemical change has taken place. We know this without the litmus test, as the sodium melted, became a globule, and finally disappeared. Heat was produced, perhaps enough to heat the water next the bead of molten metal sufficiently to make a cushion of steam, which, escaping from underneath, caused it to spin upon the surface of the water. But from the former experiment we suspect the production of a colorless gas. If now we repeat the experiment, using a pneumatic trough † and confining the sodium in a wire-gauze basket so that we may submerge the metal and convéniently collect any gas produced sufficiently insoluble in water to admit of its collection in that way, we do obtain a gas. It is colorless, like air; it is also odorless, tasteless, and only slightly soluble in water, as shown by our ability to collect it over water (1000 volumes of water

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* Litmus is a purple coloring matter extracted from certain lichens. Unsized, so-called filter or bibulous, paper is dipped into a water extract of litmus and allowed to dry.

† The pneumatic trough is a vessel used for the collection of gases over a liquid, usually water. It seems to have been invented by Hales. As some gases are soluble in water, Priestley used mercury as the liquid.

dissolve 19 volumes of the gas). However, if we remove the vessel in which the gas has been collected, having closed it with a sheet of glass, we may prove that it is not air by bringing it near a flame, when, on removing the cover, the gas takes fire and burns with a colorless flame. It may show a slightly yellow color, but that is due to the sodium present in the water.

The substance formed in the water and which turns the litmus blue is known as caustic soda, or sodium hydroxide. The chemical change, interaction, or *reaction*, as it is usually termed, may be written as follows: —

$$\text{Water} + \text{sodium} \rightarrow \text{hydrogen} + \text{sodium hydroxide},$$

or, if we use the symbols: —

$$\mathrm{HOH} + \mathrm{Na} \rightarrow \uparrow \mathrm{H} + \mathrm{NaOH}.$$

The horizontal arrow shows the direction in which the reaction proceeds. The vertical arrow pointing upwards indicates that it is a gas and escapes from the liquid. It will be observed that the sum of the atoms on one side of the horizontal arrow is equal to that on the other; hence, this is more frequently written with the equality sign (=). Such an expression as "NaOH," which indicates the presence of one atom each of sodium, oxygen, and hydrogen in the sodium hydroxide, is called a *chemical formula*. When more than one atom of an element is present, it is indicated by a numeral subscript at the right. For example, the formula of water is H_2O. In writing a formula, usually the metallic substance, or that which acts like one, is placed first. When the atoms of only two elements are present in the compound, it is binary. In naming the compound the name of the second element is modified so that it ends in "-ide," and thus becomes descriptive; for example, a binary compound of oxygen is an oxide; of chlorine, a chloride; and so forth. The whole reaction written with symbols is called a *chemical equation.* These equations are very important and are constantly used, but the impression that they constitute chemistry must be avoided. Yet they give us much information; for example, the symbols tell the relative weights of the elements entering the reaction, and it will be noted that the sums of the atomic weights on each side of the equation are equal.

$$\begin{array}{c} H_2O + Na = H + NaOH. \\ 1 \times 2 = \underbrace{\underbrace{2 + 16}_{18} \quad 23}_{41} \qquad \underbrace{1 + \underbrace{23 + 16 + 1}_{40}}_{41} \end{array}$$

Long before the conduct of steam with hot iron was understood, or the conduct of water with sodium (Davy separated the metal for the first time just a century ago) was heard of, the existence of this gas was known. It was found when Paracelsus (1493–1541) obtained an inflammable gas by the action of acids upon metals, but he did not prove that it was different from other inflammable gases. De Mayerne (1650) produced it from iron and sulphuric acid. This method for producing it is one of the few very old procedures not outgrown in the progress of chemistry and is constantly in use to-day. Such a process we may illustrate in —

Experiment III. Zinc + hydrogen chloride = hydrogen and zinc chloride:

$$Zn + 2\,HCl \overset{\rightarrow}{=} \uparrow H_2 + ZnCl_2.$$

In this equation we have another feature illustrated. When several molecules of one kind are involved in a reaction, we indicate the number by a figure placed before the entire formula of the substance. For example, 2 HCl means that two hydrogen chloride molecules are necessary, and that not only two hydrogen but two chlorine atoms are present. We also note that hydrogen is combined with one chlorine atom, whereas zinc combines with two.

The gas is the lightest substance known. Some volcanic gases contain it, but it diffuses more rapidly than any other gas, so it is found free in the air in extremely small amounts (less than 1 in 30,000). It is found in small cavities in a few rare minerals. The spectroscope shows its presence in the sun. It is 14.39 times lighter than air. It therefore has a specific gravity of 0.06949. One liter at 0° * and under 760 mm. pressure weighs 0.089 g., equal to one *crith*. One gram of it will fill 11.12 l. at zero and under normal pressure. It may be collected by upward displacement. It is a good conductor of heat, but a poor conductor of sound. By cooling to − 243°, it has been converted into a liquid with a specific gravity of 0.07 at that temperature. At − 255° it becomes a white crystalline solid (Dewar). These characteristics are designated as the *physical properties*.

It burns in the air with a non-luminous flame (philosopher's or Döbereiner's lamp), producing moisture (Macquer, 1766). Cavendish and Watt (1781) also observed the production of water when the gas was burned in air. Lavoisier (1783) named it hydrogen, from ὕδωρ γεννάειν (to produce water).

Hydrogen has a strong affinity for what are called negative elements. It combines with oxygen and chlorine, under proper conditions, with explosive violence and the

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* All temperatures in this book are centigrade (C.) unless stated otherwise.

generation of heat. More heat (68,000 calories) is produced when hydrogen is burned in oxygen than in any chemical reaction known. It shows little tendency to combine with electro-positive (metallic) elements, yet it does form such compounds as LiH_2, Na_4H_2, K_4H_2. Palladium can condense 980 times its volume of hydrogen, and the latent heat made sensible in this apparent change from the gaseous to the solid state is sufficient to cause it to combine with oxygen. Finely divided platinum will also do this. These characteristics are known as *chemical properties*.

In the free condition it is not poisonous, but when breathed it weakens the voice and gives it a higher pitch.

It occurs in all acids, is combined with oxygen in water, combined with carbon in natural gas and petroleum, and with carbon, oxygen, and other elements in all living matter.

The production of so much heat during its combustion is utilized in the oxyhydrogen lamp for lead burning, the smelting of platinum, producing the lime-light, and so forth. Numerous technical processes for its production commercially, as heating carbon with slaked lime, and freezing the other gases out of producer gas by means of liquid air, have met with failure. An alloy of sodium with lead ("hydrone"), when in contact with water, generates hydrogen most satisfactorily.

If we place the terminals of a direct current of electricity in pure water, no evidence of a flow of electricity is observed. If the water has an acid, that is, a sour substance, added to it, the current passes. This is shown not only by electrical instruments, but by the escape of gases at each terminal. If these gases are collected with suitable apparatus, we observe that both are colorless and odorless, but one has twice the volume of the other. On testing the one with the larger volume, we learn that it is hydrogen. The other we shall study in the next chapter.

EXERCISES

1. Give the typical methods used in making hydrogen and emphasize the important features.

2. Why may hydrogen be collected by upward displacement? What is meant by the diffusion of gases and what laws govern it?

3. What do the following two equations tell from the principles already presented?

(1). $Mg + 2\,HCl \xrightarrow{} MgCl_2 + \uparrow H_2$;

(2). $Zn + 2\,NaOH \xrightarrow{} Na_2ZnO_2 + \uparrow H_2$.

(Refer to table, p. 18.)

CHAPTER IV

OXYGEN — OZONE

OXYGEN, O. At. Wt., 16. M. Wt., 32

FOR several centuries it has been known that a portion of the air is fixed by certain metals when they are heated in it (Jean Rey, 1630). Some metals fix a part of the air on exposure to it, without evidence of measurable heat; for instance, iron rusts in the air. Mayow (1674) obtained a gas which he called "nitro-aerial spirit," by heating niter. Scheele (1771–1777) prepared "aer vitriolicus," "fire air," or "life air," by heating several oxygen compounds, among them black oxide of manganese. To Priestley (1774), however, is given the honor of discovering that part of the air which is fixed by metals. In accord with the nomenclature of the day, he called it "dephlogisticated air." He obtained it by heating mercuric oxide (Experiment III, Chapter I) with sunlight concentrated by a lens. Lavoisier (1774–1781) explained its relation to oxidation, combustion, and respiration. Considering it an "acidifying principle," or constituent of all acids, he named it *oxygène* from *ὀξύς γεννάειν* (to produce acid).

It occurs (I) free and (II) combined.

I. It constitutes one fifth by volume and one fourth by weight of the air.

II. (*a*) As oxides: water, H_2O; silica, SiO_2; iron oxide, Fe_2O_3; carbon dioxide, CO_2.

(*b*) In compounds with two or more other elements, called salts: limestone (calcium carbonate), $CaCO_3$; heavy spar (barium sulphate), $BaSO_4$; mica (potassium aluminum orthosilicate), $KAlSiO_4$.

(*c*) It is a component of most animal and vegetable matter, as urea (CON_2H_4) and sugar ($C_{12}H_{22}O_{11}$).

It is the most abundant of all the elements, forming about one half of all the matter of the earth's surface.

Oxygen is prepared by a number of different ways. Five different methods are given, as each one illustrates a principle.

First, by heating certain oxides, as

$$2\ HgO \leftrightarrows 2\ Hg + O_2 \text{ (above } + 300^\circ\text{)},$$

and

$$BaO_2 \rightleftarrows BaO + O \text{ (above } + 1000^\circ\text{; reforms at } + 500^\circ\text{)}.$$

Second, by the electrolysis of water: —

$$2\ H_2O \rightleftarrows 2\ H_2 + O_2.$$

Third, by heating certain salts which contain a large proportion of oxygen, as potassium chlorate:

$$2\ KClO_3 \overset{\rightarrow}{-} 2\ KCl + \uparrow 3\ O_2.$$

This reaction takes place best at + 350°, but with greater smoothness and at a lower temperature (+ 200°) when some manganese dioxide is added.

Fourth, from liquid air.

Fifth, very conveniently, by treating sodium dioxide ("oxone") with water:

$$2\ Na_2O_2 + 2\ H_2O \overset{\rightarrow}{-} 4\ NaOH + \uparrow O_2.$$

Physical Properties. It is a colorless, odorless, tasteless gas, with a specific gravity of 1.1056 and a density of 15.89. One liter at zero and 760 mm. pressure weighs 1.429 g. One hundred volumes of water dissolve 4 volumes at zero and 3 volumes at +15°. One hundred volumes of absolute alcohol dissolve 28 volumes of oxygen. It boils at −184°. The liquid, which is of a bright blue color, has a specific gravity of 1.124 at −184°. Its critical temperature is −118° and critical pressure 50 atmospheres.

Chemical Properties. It is non-combustible, but is a powerful supporter of combustion. The combustion usually occurs with the production of much heat and often light. Oxygen compounds are known of all the elements, except fluorine, bromine, and the inert elements (helium, argon, neon, krypton, and xenon). Elements combined with oxygen alone give compounds called *oxides.*

The burning of ordinary substances in the air, as wood and coal, is dependent upon the presence of oxygen in the air. Substances burn in pure oxygen much more rapidly and with more brilliance. The slow combination of oxygen with substances is spoken of as *oxidation,* rapid combination as *combustion.* When we add oxygen in chemical union to a substance, we *oxidize* it. Iron takes oxygen from the air slowly in rusting. It does the same thing, but more rapidly, in pure oxygen at a low temperature. If heated first, it burns with great brilliancy, with the production of much heat. Just as much heat is produced in the three cases, but in the former two it is dissipated on account of the time factor, hence is not measurable. In the three cases the iron is oxidized.

Uses. Oxygen is used extensively for the production of heat in all processes of combustion. Oxygen may be breathed in the pure state for a time without injury, but the life forces acquire very much greater activity. Too long breathing of oxygen causes rapid cardiac action and the production of febrile condition. It is used in medicine for the treatment of pneumonia and anæmic conditions.

OZONE, O_3. M. Wt., 48

Schönbein, in 1840, accounted for the peculiar odor which is produced when an electric spark passes through oxygen or the air by the formation of ozone. The odor had been detected by Van Marum in 1785.

Preparation. It is prepared by the passage of electricity through moist oxygen (up to about 5 per cent); by the slow oxidation of some substances, as phosphorus; and recently in a more concentrated form by the action of ultra-violet light of wave lengths of 260 $\mu\mu$ and shorter.

It is found in the oxygen given off by plant leaves; is produced in the oxidation of turpentine and probably by the beating of ocean waves upon the shores; and by electric disturbances in the air. It readily decomposes into oxygen, but is sometimes found to the extent of 0.1 mg. in 100 l. of the air.

Properties. It is a gas which possesses a peculiar odor, and in thick layers has a bluish color. Under a pressure of 150 atmospheres or when cooled to − 184°, it condenses to an indigo-blue liquid (b.-p. − 116°). It is fifteen times as soluble in water as oxygen. At + 250–300°, or when exposed to light of wave lengths longer than 300 $\mu\mu$, it is changed back to oxygen. It is half again as heavy as oxygen (sp. gr. 1.66). It is a powerful oxidizing agent, being known for a while as "active oxygen." It oxidizes silver, which is unaffected by ordinary oxygen. It turns starch iodide paper blue, due to the liberation of free iodine by oxidation, which reacts with the starch to produce the color. It bleaches many dyes, which ordinary oxygen does not. When strong it irritates the air passages, even producing severe catarrh. Dilute, it serves to destroy organisms, hence purifies the air.

It is used diluted, as found naturally in turpentine and hemlock districts, and is also artificially made in some urban sanatoriums, for the treatment of pulmonary diseases. In a concentrated form it serves to bleach oils and starch, sterilize drinking water, and assist in the disposal of sewage.

From the facts that ozone is made directly from oxygen, ozone decomposes to form oxygen, and is half again as heavy, we assume that its molecule is composed of three atoms, at least, of oxygen. This requires an assumption, which later will be shown to be correct, of the presence of two atoms of oxygen in a molecule of oxygen. When an element exists in two or more forms, as illustrated here and elsewhere (Chaps. XII, XVIII), the phenomenon is a case of *allotropism*. Usually there are some energy demonstrations in the changes from one form to the other. For instance, heat is absorbed when oxygen is converted into ozone (endothermic) and is evolved in the reverse process (exothermic): —

$$3\ O_2 = 2\ O_3 - 32{,}400 \text{ calories.}$$

Inasmuch as we may cause oxygen to form ozone or ozone to form oxygen, the reaction is spoken of as *reversible*, and may be indicated, $3\ O_2 \rightleftarrows 2\ O_3$. Many reactions are reversible.

EXERCISES

1. What are the principles illustrated by the methods given for the preparation of oxygen?

2. What is meant by an oxide? oxidizing a substance?

3. Why do we say that the same amount of heat is produced in the combustion of iron in oxygen and in the formation of rust, assuming that the product of the former reaction is the same as rust?

4. Why may we assume the presence of at least two atoms in the molecule of oxygen?

CHAPTER V

WATER

H_2O. M. Wt., 18.016

HYDROGEN unites with oxygen to produce water. It occurs naturally in familiar abundance and widely distributed, covering the larger portion of the earth and penetrating its crust. It occurs as vapor in the air, from which it is condensed as dew or precipitated as rain, snow, and so forth. It constitutes a part of many minerals and chemicals. Three fourths of all living matter are water. In fact, it is absolutely necessary for the world's continuance as a habitable globe for us. An acre of green plants may evaporate 150 tons of water in a season. It is the best known chemical compound and essential for many chemical changes. Its study is therefore of the utmost importance from a scientific, as well as practical, standpoint.

Water, as ordinarily seen, especially as a deep layer in large bodies, has a blue or greenish blue color. Such water is impure. It is purified by *distillation.* The apparatus used for making *distilled water,* which is pure enough for ordinary laboratory purposes, is constructed of tin, copper, or glass. The purest water cannot be kept for any length of time in glass vessels, because some of the constituents of glass are dissolved, and they render the water impure. The purest water is made in apparatus constructed of materials the least affected by water, for example, platinum or quartz. The first portion of the *distillate* is discarded, and only the middle portion is collected.

Pure water is a colorless liquid between 0° and + 100° and has an insipid taste. As the temperature is lowered it becomes denser, showing the greatest density at + 4°; below that point it expands till it freezes at zero. This is the reason why water freezes at the top and not the bottom of our lakes and streams; for the water, being less dense at the freezing point than at + 4°, remains on the surface. When water changes into ice, 100 volumes of water expand to 109 volumes of ice (sp. gr. 0.9173), which floats. Water crystallizes in rhombohedra of the hexagonal system. Under a pressure of 1000 atmospheres water solidifies at − 7°. Water begins to dissociate into hydrogen and oxygen at + 1000°; the dissociation is complete at + 2500°. One volume of water at + 100° is changed into 1696 volumes of steam. The specific gravity of steam is 0.622. One liter of aqueous vapor at + 100° and 760 mm. pressure weighs 0.59 g. The latent heat of ice is 79 calories; the latent heat of steam 536.4 calories.

In studying the composition of any substance, we have four objects in view; namely, to learn (1) of what it is composed, that is, its *qualitative* composition; (2) how much of each element is present, that is, its *quantitative* composition; (3) how many atoms are in the molecule, that is, the *molecular weight;* and (4), if it is a compound, how the atoms are associated in the molecule.

At this point in determining the composition of water, it is convenient to consider only the first two objects. It is desirable, almost necessary, before drawing final conclusions, not only to analyze, but to synthesize a substance as well. The study of the composition of water is given in some detail as an illustration of methods of procedure in scientific investigations.

Qualitative Composition

First, we have seen that metals break up water and give off hydrogen.

Second, by the electrolysis of water, we obtain hydrogen and oxygen. As pure water has not been decomposed by the electric current, these gases might be attributable to the acid or alkali added (in fact, we know they are not); but,

Third, hydrogen when burned in oxygen forms water.

Therefore, it appears that water contains only hydrogen and oxygen. To prove it, however, we determine its

Quantitative Composition

First, by electrolysis, we learn that we obtain two volumes of hydrogen and one volume of oxygen from water:

$$\text{Water} = 2\ \text{H} + 1\ \text{O}.$$

Second, if we mix two volumes of hydrogen and one of oxygen and cause them to combine by passing an electric spark through the mixture, we obtain water. If we have an excess of either gas beyond this ratio, 2 : 1, that excess remains in the apparatus unchanged (law of definite proportions). We may weigh the gases and thus determine the weights of each involved in the synthesis, but it is an inconvenient and difficult procedure. We therefore confirm the above,

Third, by passing hydrogen, free from water, over a metallic oxide which is heated. Black copper oxide, when treated in this manner, gives up its oxygen to the hydrogen, forming water, and assumes the color characteristic of metallic copper:

$$\text{Copper oxide} + \text{hydrogen} = \text{water} + \text{copper}.$$

If we subtract the weight of copper after the experiment from the weight of the copper oxide before the experiment, we obtain the weight of the oxygen taken by the hydrogen to form the water. This weight subtracted from the weight of the water collected gives the weight of the hydrogen necessary to combine with the oxygen to produce that amount of water. The data thus secured show us that eight parts by weight of oxygen combine to form nine parts by weight of water. One part by weight of hydrogen is needed, and the ratio by weight of oxygen and hydrogen in water is 8 : 1. But we have seen that two volumes of hydrogen combine with one volume of oxygen to produce water, and it is necessary for us to harmonize these facts in any interpretation we may make.

From the gas laws we know that all gases, within reasonable limits, expand or contract for equal increments of heat and similar variations in pressure. Therefore, gases exist as free-moving molecules, and equal volumes of gases under like conditions of temperature and pressure contain an equal number of molecules. This is the reasonable explanation offered by Avogadro in 1827. It matters not what is the composition of the molecules, whether they are single atoms or contain a large number of atoms.

The simplest assumption regarding the hydrogen molecule, and so far data have not been presented in these pages which warrant any other, is that it contains one atom. As two volumes of hydrogen require only one volume of oxygen to produce water, the ratio becomes a multiple; that is, 2 : 16 instead of 1 : 8. By definition half atoms cannot enter our considerations, and as we have learned (p. 33) that the oxygen molecule contains at least two atoms, we conclude that the oxygen atom bears an *equivalent* weight relative to the hydrogen atom of 8 : 1. If, by convention, the lightest known atom (hydrogen) is placed at 1, we may say that the atomic weight of oxygen is 8. In fact, using round numbers, it is 16. The reasons for arriving at the latter figure, which is now given to avoid a temporary wrong impression, will be seen later (p. 52).

EXERCISES

1. Upon what theoretical considerations does the distillation of water depend? Why should the first portion of the distillate be discarded in preparing the purest water?

2. Why do lakes and other natural bodies of water freeze at the top?

3. How is the composition of water proven?

4. How much copper oxide would be used and copper obtained in preparing 3.2 g. of water?

CHAPTER VI

WATER — PRACTICAL CONSIDERATIONS

WATER is nature's great solvent. All substances are more or less soluble in it. Therefore, when naturally found it is never pure. Rain-water contains dust, nitrogen, oxygen, and carbon and other compounds, many of which are fortuitous. Much of it sinks into the earth and issues again in the form of springs and rivers, containing different mineral constituents, depending upon the minerals with which it has come in contact. Hard water, — temporary and permanent, — contains calcium and magnesium salts. The waters from mineral springs are given names according to certain constituents which they may contain, as iron (chalybeate), alum, hydrogen sulphide (sulphur), salts (saline), lithium compounds (lithia), carbonic acid (acidulated), and so forth. Waters with these various constituents eventually reach the oceans or some inland lake. There they evaporate with a constant accumulation of the non-volatilized solids, for the evaporated water is again precipitated, as rain, snow, and so forth, scours the land, and returns to the oceans laden with another burden of variegated suspended and dissolved matter. Sea water contains 2.7 per cent of sodium chloride (salt) with a total of 3.5 per cent of solid matter. Some of the salt lakes contain a much larger percentage.

In making steam these solids accumulate within the boilers and constitute a frequent source of grave annoyance unless removed. They sometimes form solid cakes and produce what is known as boiler scale. The scale is not a good conductor of heat, so the efficiency of the boiler is affected, often seriously. The metal and the scale have different coefficients of expansion. If the water gets too low in the boiler, the metal becomes overheated and expands away from the hard scale, which often cracks. If fresh water is run into the boiler, the scale, quickly cooled, cracks and brings water directly in contact with the superheated metal and underneath the scale. A large volume of steam is suddenly generated, some of the water even being decomposed perhaps. Unusual pressure is produced, often with consequent explosion.

The most important practical problem for any community is the provision of a satisfactory supply of potable water. With congestion of population filth accumulates on and in the soil. Water which has come in contact with these sources of contamination and is subsequently drunk propagates disease. Mortality diminishes when potable water is supplied, but increases after an interval unless provision is made for the disposal of the sewage.

Three factors are involved in determining the potability of a water and accepting it as a constant supply. First, regular bacteriological examinations should be made to determine the presence of pathogenic (disease-producing) bacteria. Second, frequent chemical examinations of the water should be made to determine the presence of food (nitrogenous organic compounds) upon which the bacteria live and propagate. The bacteria cannot exist long in media which are not provided with their food. The determination of their presence in water one day does not indicate their continuance, unless the chemical examination shows the presence of their food. A chemical examination may show the presence of bacterial food and also products resulting from their thriving upon that food (presence of free ammonia, nitrites, and nitrates), which means that the water is suspicious and should be avoided, but it does not prove that the bacteria present are disease-producing. There are beneficial bacteria and harmful bacteria. The former cause, through processes termed *nitrification* (oxidation) and *denitrification* (reduction or de-oxidation), the complicated carbon compounds of nitrogen in water and the soil to be reduced to simpler compounds, harmless in their diluted condition, as far as the production of disease is concerned, and most useful, in fact essential, in providing food for plants. This shows how closely chemistry and biology are associated. Third, a regular systematic survey should be made of the sources from which the water is obtained. By these means a temporary or permanent contamination of the water may be determined and proper steps taken to avoid the evil consequences of using it. No citizen can have these facts too well impressed upon him. He need not, however, concern himself with the details by which the information is obtained, for they involve technicalities known only to the expert in such matters.

As an adequate supply of water sufficiently pure is difficult to secure for a large community, except at great expense, it becomes necessary at times to use a fairly impure water and render it potable. Most bacteria, or their spores, cease to live at the temperature of boiling water. It is safe, therefore, when the potability of water is in question, to boil it. Doing this on a large scale, however, is out of the question on the score of the expense involved.

Water may contain suspended or dissolved impurities. The former are removed by filtration, provided the pores of the filtering medium are sufficiently small. A Pasteur filter is made of unglazed porcelain and has very small pores. When this is attached to the pipe, the water is forced through by its own pressure and the fine particles are held back. These soon form a slimy coating which practically prevents the passage of the liquid. This slime may also become a breeding bed for the bacteria, so it should frequently be removed and cleaned. On a large scale the filter is usually made of sand, the grains of which, lying upon each other, give considerable porosity. Very finely divided particles (clay soil is made up mainly of particles less than 0.005 mm. in diameter) are often not removed when water passes through a sand filter; nor are the bacteria, which are even smaller. A jelly, which is more or less agglomerated, does not pass through the pores. If we agitate the water with a gelatinous material, these particles, even the bacteria, are more or less attached and then are held back by the filter. This is accomplished practically by adding something to the water which subsequently forms the desired jelly. Alum is a compound of some complexity, which on being added to water in small amounts *dissociates*, that is, breaks up into simpler substances. As water brings about this *dissociation*, we speak of the phenomenon as *hydrolysis*. It plays a very prominent part in many chemical actions. One of the dissociation products of alum is a white jelly [aluminum hydroxide, $Al(OH)_3$].

Another method of treating water is to impound it and make the conditions most favorable for the propagation of the bacteria. They develop very rapidly and soon exhaust the food available, producing harmless substances, and die through starvation. Or, the bacteria are killed by the addition of a poison (in very small amounts), which, after it has done its deadly work, gradually decomposes or combines with something else. Water so treated becomes harmless when taken into the animal system. Some of the substances used for this purpose are ozone, chlorine, and copper sulphate. The last named has recently come into extensive use, as it also kills certain vegetable growths (algæ). These plants grow in abundance in some ponds or lakes, where drinking water is collected, and often give the water objectionable color or odor or taste, and produce disease.

EXERCISES

1. Explain the formation of boiler scale.

2. Outline the main considerations involved in determining the potability of water.

3. Give and explain the principles put into practice in rendering water potable.

CHAPTER VII

WATER — THEORETICAL CONSIDERATIONS

When a gas is liberated in a closed vessel which has been evacuated, it spreads itself throughout the volume of the containing vessel. It occupies the space, as it were, and exerts a pressure upon the restraining walls. All gases do this, it matters not what is the composition of the molecules. The distribution is uniform, and presumably the same number of molecules are in equal volumes (Avogadro's hypothesis). Similar conditions of temperature and pressure must obtain, to be sure, but the gas retains its chemical individuality. When we bring together two volumes, one each, of different gases, which do not form a chemical combination under the prevailing conditions, we find that the particles of each gas distribute themselves uniformly through the new volume. The mixed gases exert a combined pressure, made up of the pressures of the two, acting independently of each other. Each gas therefore exerts a *partial pressure.*

When we place a solid (salt) in a liquid (water), there is a tendency on the part of the solid particles to enter the liquid. The pressure created by the molecules of the solid is known as *solution pressure.* A time arrives when this pressure is equaled by the pressure created by the particles in solution trying to return to the solid. There is equilibrium at that temperature. The excess of the solid remains behind, and we have a *saturated* solution. The solute distributes itself uniformly throughout the volume of the solvent, so the liquid acts as a medium through which the molecules occupy the volume of the liquid. The solubilities of different substances are not the same, hence we do not get the same number of molecules in equal volumes of the saturated solutions of different substances. To be sure, we do get a definite quantity of the solute in solution for each temperature,* but this quantity bears no atomic relationship to the solvent, hence we do not look upon the solution as a normal chemical action which involves breaking into the molecule. Yet the physical individualities of the substances dissolved are sometimes changed. Also in particular cases we do get a change, such as we observe in hydrolysis.

In a measure, the presence of one solute does not interfere with the presence of another. We may mix a saturated sodium chloride solution with a saturated sodium carbonate solution, both in water. Or, putting it another way, if we have one solution, say, of sodium chloride about half saturated, and place in it an excess of the carbonate, the liquid will take up enough of the carbonate to saturate that part of the water beyond the amount necessary to make a saturated chloride solution for the amount of chloride present. Each exerts its partial pressure, as in the case of the gases.

The solubility of a solute in different solvents is usually different. If, therefore, we have two immiscible solvents mixed, the solute distributes itself in each, according to the specific solution tension. An illustration will make this clear. Iodine is not very soluble in water, yet we may

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* In some cases we obtain a liquid which has in solution more of the solute than it normally holds at the special temperature. This we call *supersaturation.* The solution is in unstable equilibrium. As soon as the liquid is disturbed, by the introduction of a tiny crystal or a particle of dust, the excess of the solute separates at once.

make a saturated solution. Iodine is very soluble in ether. Water and ether are so limited in their solubility in each other, that we say they are immiscible. If we mix the water solution of iodine with ether, most of the iodine goes into the ether, but not all. The iodine distributes itself according to its solution pressure with each solvent (*Law of Partition*). This process is called *extraction*, and is one extensively used in chemical practice.

Each solvent dissolves a definite amount of each solute at a fixed temperature. The amount of gas dissolved decreases with the elevation of temperature. The reverse is usually the case with solids; for example, 100 parts of boiling water dissolve 360 of alum, whereas 100 parts of cold water dissolve only 10 parts of alum. If a saturated solution is made at + 100° and then is cooled to a lower temperature, the excess above the amount equal to the solubility at the lower temperature will ordinarily separate out, in this case, as crystals. The molecules must be in a mobile condition, and when they have time for settling, they tend to arrange themselves into masses often bounded by definite planes which form regular angles.

The phenomenon of *crystallization* may be brought about by (1) evaporation of a portion of the solvent, (2) by melting a solid without using any solvent, or (3) by sublimation. The essential conditions are freedom of movement of the particles and time for their assumption of definite forms.

There are six basic forms according to which crystals are classified:—

1. Regular or isometric system with three axes, all equal and at right angles to each other.

2. Quadratic or tetragonal system, one of the three axes is of a different length.

3. Rhombic, all axes unequal but at right angles.

4. Monoclinic, all axes unequal, only two at right angles.

5. Triclinic, all axes unequal, all oblique, none at right angles.

6. Hexagonal, three axes in one plane forming equal angles (60°), a fourth at right angles to that plane.

By the evaporation of simple solutions we recover the solute, in some cases unchanged. In others all the solute is there, but it has appropriated a definite amount of the solvent, which gives the residue properties different from those of the original solute. Hence, in the simple solution we may have indications of physical and chemical changes. An illustration will render this clearer. When water is the solvent and salt is the solute, on evaporation we obtain the crystals characteristic of the sodium chloride. If we dissolve dry soda (sodium carbonate) in water and evaporate the solution, we get crystals composed of soda plus ten parts of water. By slight heat the water is driven off and the clear crystals immediately crumble into a powder, the same as originally dissolved, and give the appearance of losing their crystalline form. A more striking illustration is had when a solution of copper sulphate (bluestone) is evaporated. Large blue crystals are obtained, which contain hydrogen, copper, oxygen, and sulphur in the proportion to give the formula $CuH_{10}SO_9$. In making the analysis, however, it is observed that by heating we may drive off hydrogen and oxygen to the extent of $5\ H_2O$ and collect it directly as water. The blue color of the crystal disappears. For these reasons, namely, loss of crystalline form, color, and so forth, the water present has been commonly referred to as *water of crystallization*, and the formula of this particular substance may be written, $CuSO_4$, $5\ H_2O$.

In point of fact, this is incorrect, because the water present is just as much a part of the molecule as the soda or copper sulphate. When the water is removed in part or entirely, the particular crystalline form is changed. Progressive thought teaches that all solids are crystalline. We do have solids which appear without crystalline form, —*amorphous* substances,—but they are supercooled liquids. The water taking part in the formation of a definite crystal form enters as a molecular compound. These compounds may properly be spoken of as *hydrates*.

There are other substances which, when dissolved in water, combine with it in a different manner from that just referred to. We may illustrate this by an example, but a study of the substances involved must be postponed to a more appropriate time. Sodium oxide dissolves in water according to the formula,

$$Na_2O + H_2O \rightleftarrows 2\ NaOH,$$

and we have a real chemical solution, for on evaporation we secure the solid NaOH or 2 NaOH. The NaOH dissolves, however, forming a simple solution. On account of the OH, these compounds of water are called *hydroxides* (a word derived from hydrogen and oxygen). This particular one (sodium hydroxide) does not yield water on heating, but many of them do; for example,

$$2\ CuOH \rightleftarrows Cu_2O + H_2O.$$

Although we obtain water on heating hydrates and hydroxides, the water is present in an extramolecular union in the former and intermolecular union in the latter.

The particles of evaporating water pass off in the gaseous state. This is a property of all liquids. The rate at which the particles leave is defined by the gaseous pressure they exert and is known as the *vapor pressure* of the substance under the particular conditions. If a vessel is partially filled with a liquid and closed, the vapor pressure soon reaches a maximum, which is definite for each temperature. The pressure is independent of the amount of liquid present, provided there be enough to produce sufficient vapor to create the pressure for the particular temperature. If there is too little of the liquid, it is all changed into a gas and the maximum pressure is not attained. If the gas above the liquid is compressed, the temperature remaining constant, a portion at once returns to the liquid state, as more than the maximum pressure cannot continue. The pressure of the gas is dependent upon the number of molecules in each unit of space. The pressure increases with increase of temperature. The maximum pressure at any temperature is known as the *vapor tension* of the liquid at that particular temperature. Aqueous tension at 0° will support a column of mercury 4.6 mm. high; at 20°, 17.4 mm.; and at 100°, 760 mm., when the water boils. When water is under an atmospheric pressure of 680 mm., it boils at + 97°; 800 mm., at + 101.4°. When the space above water has taken up all the vapor allowed by the aqueous tension at a particular temperature, it is said to be saturated. It will thus be seen that the aqueous tension is independent of the size of the space and the amount of water, provided there is an excess. It is even independent of the presence of other gases, and is dependent solely upon the ability of the water to produce a vapor. The *humidity* of the air varies. It is usually about two thirds saturated.

Solid hydrates, as those referred to, tend to give off the combined water in the form of a vapor, as ice does.

Crystals of sodium carbonate with ten molecules of water, or sodium sulphate with ten molecules of water (Glauber's salts), on exposure to the air lose water and crumble down to a white powder. We speak of this as *efflorescence.* If the crystals are placed in a stoppered bottle, they continue to give off water. After a lapse of time, however, the vapor pressure reaches the maximum, and no more water is given off. The crystals retain their characteristic form. Each hydrate possesses a definite vapor pressure.

When the vapor tension is less than the aqueous tension of the air, the crystal retains its form. As stated, the aqueous tension at 20° is 17.4 mm., and ordinarily the pressure in the air is about 12 mm. (two thirds). Copper sulphate with five molecules of water exerts a pressure of 6 mm. at 20°; consequently, its crystals remain unchanged on exposure to the air.

EXERCISES

1. Trace the relationship between the partial pressure of gases and the solution pressure of solids.

2. Explain the law of partition.

3. What are the six basic forms of crystals and the conditions favorable for crystallization?

4. What is the explanation of vaporization, and upon what factors is it dependent?

5. Explain what is meant by a hydrate; hydroxide; efflorescence.

CHAPTER VIII

THE HALOGENS

THE solid obtained from evaporated sea water is a mixture of a number of compounds, the most prominent of which is sodium chloride. When this is treated with an acid, as sulphuric, a gas is given off, a water solution of which is known as hydrochloric acid (see next chapter). The gas is hydrogen chloride.

If hydrogen chloride is liquefied and has a direct current of electricity passed through it, two gases of equal volumes are obtained. One is colorless hydrogen, evolved at the negative pole; and the other is yellowish green chlorine, given off at the positive pole. Although it was discovered by Scheele in 1774, Humphry Davy proved the elementary nature of chlorine in 1810 and named it.

If hydrogen and chlorine are brought together, they unite with explosive violence (either when heated or on exposure to bright light) to re-form the hydrogen chloride. We find one volume of hydrogen requires one volume of chlorine. After the union we have two volumes of the hydrogen chloride.* Gay-Lussac (1808) laid down a simple *law of combining volumes*; namely, *whenever gases unite, or whenever gaseous products result from the union, the volumes involved can be represented accurately by ratios of small integers.*

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* The measurements are made under similar conditions of temperature and pressure, and unless otherwise stated all measurements of gases are to be considered as made at 0° and 760 mm. pressure.

This may be readily illustrated by diagrams: —

$$\boxed{\begin{array}{c}\text{1 volume}\\ \text{hydrogen}\end{array}} + \boxed{\begin{array}{c}\text{1 volume}\\ \text{chlorine}\end{array}} = \boxed{\begin{array}{c}\text{2 volumes}\\ \text{hydrogen chloride}\end{array}}$$

and

$$\boxed{\begin{array}{c}\text{2 volumes}\\ \text{hydrogen}\end{array}} + \boxed{\begin{array}{c}\text{1 volume}\\ \text{oxygen}\end{array}} = \boxed{\begin{array}{c}\text{2 volumes}\\ \text{water (steam)}\end{array}}$$

The ratios for hydrogen chloride are 1 : 1 : 2, and for water 2 : 1 : 2.

According to the explanation of Avogadro, and we have no better, we have equal numbers of molecules in equal volumes of gases (under the same conditions of temperature and pressure). If we assume that each single volume contains 1000 molecules, then we have 2000 molecules of hydrogen chloride. There can be no case of partial pressure (*q.v.*) here, as chemical combination has taken place. The composition of hydrogen chloride calls for at least one atom each of hydrogen and chlorine, as half atoms are excluded by definition. As there are 2000 molecules of hydrogen chloride, there must be at least 2000 atoms of hydrogen in the 1000 molecules of hydrogen. Hence, each molecule of hydrogen must contain at least two atoms. The same is true for the chlorine and oxygen. Therefore, we confirm the statement that the atomic weight of oxygen is 16, not 8, and we may write the formula for the electrolysis of hydrogen chloride: —

$$2\,HCl \rightleftarrows H_2 + Cl_2.$$

This is one of the methods by which the number of atoms in a molecule may be determined. It is applicable only to the gaseous state, however.

In order to eliminate intermediate steps from the raw product to the finished material, practical men applied the principle of electrolysis directly to the sodium chloride in solution: —

$$2\ NaCl \rightarrow Na_2 + Cl_2.$$

The reaction is, in fact, more complicated than shown in this equation, but chlorine is now obtained free in large quantities in this manner.

Of considerable historical interest and theoretical importance is the method used by Scheele in the discovery of chlorine. If hydrogen is removed from hydrogen chloride, chlorine is obtained free. In oxidizing a substance, at one time, we were supposed to introduce oxygen into the compound. We may oxidize a substance, however, by taking hydrogen away from it. We know that hydrogen readily combines with oxygen, so we may oxidize hydrogen chloride with an agent like manganese dioxide. We get an equation: —

$$x\ HCl + y\ MnO_2 = z\ H_2O + w\ MnCl_2 + a\ Cl.$$

We must learn certain facts by actual experimentation before we can write out what takes place in any chemical reaction. After we have learned how many reactions proceed, we may predict, often with accuracy, the course of an unknown reaction. We may study this particular equation and opportunely learn a method by which an equation may be determined. From the experiment we know that a mixture, as shown on the left side of the equation, gives us the three substances shown on the right. We should anticipate this, because MnO_2 decomposes on heating, giving off oxygen. Scheele, in 1775, prepared oxygen in this manner. We should expect a compound like MnO_2, in which all the oxygen had been replaced by chlorine, to break up with the separation of the latter element. That fact is stated in the equation. But how much of each constituent takes part? We have learned that 2 H combine with 1 O in water (H_2O). For all the O in 1 (y) MnO_2, we require 4 H. The value of z becomes 2. In hydrogen chloride we have one each of H and Cl. Therefore, $x=4$. If we analyze the manganese chloride obtained, we secure the formula $MnCl_2$. As only 1 Mn enters, $w = 1$, and as 4 Cl are involved, we have two left over, which gives our value for a. Hence we write the equation:—

$$4\ HCl + MnO_2 \xrightarrow{} 2\ H_2O + MnCl_2 + \uparrow Cl_2.$$

The principle of oxidation is extensively used in chemical processes. Many other oxidizing agents have been and are used for the preparation of the chlorine from HCl, but the reactions are quite complicated. One of the simplest, as it appears in the following equation, is to use oxygen itself:—

$$4\ HCl + O_2 \rightleftarrows 2\ H_2O + 2\ Cl_2.$$

Chlorine decomposes water, especially under the influence of light, according to the above equation, reading from right to left. The double arrow indicates that we are dealing with a *reversible reaction* — one preponderating to the right under certain conditions and the left under another set of conditions. In order to cause it to go from left to right, it is necessary to have the proper conditions and something there to do it. In this particular case, it is necessary to have a temperature between 370° and 400°. The material used is pumice (to present a large surface), which has been soaked in a solution of copper chloride. Any material which by its presence facilitates a reaction in any one direction is spoken of as a *catalytic agent.* The process is called *catalysis.* The contact agent (catalyzer) may or may not undergo change while the reaction is in progress, but it retains its initial integrity at the end of the reaction. Catalysis plays a very important part in many chemical changes.

Along with the chlorides are similar compounds of bromine and iodine, but in very much smaller amounts. Certain plants, like seaweed, concentrate iodine. In fact this occurrence led to its discovery by Courtois, who used the ashes from burned sea-weed in making soap. In 1895 Bauman found 9 per cent of iodine in the purified extract from the thyroid gland.

Bromine and iodine are prepared by any of the methods given for chlorine, but more usually by the manganese dioxide process. As chlorine, bromine, and iodine separate at the positive pole, they are electro-negative, but to different degrees. Chlorine is more strongly electro-negative than bromine, as that element is correspondingly stronger than iodine. The more pronounced electro-negative element will displace the weaker. This fact is taken advantage of in separating these elements.

$$2\ NaBr + Cl_2 \rightleftharpoons 2\ NaCl + Br_2,$$

and

$$2\ NaI + Cl_2 \rightleftharpoons 2\ NaCl + I_2.$$

These equations illustrate the principle of *substitution,* which is extensively applied in chemistry.

The comparable properties of these three elements are given in the table. All have characteristic, penetrating, disagreeable odors. With increase in atomic weight the physical state, at ordinary temperatures, changes from that of a gas to a solid. Chlorine is soluble in water, hence is collected by air displacement. The "solid bromine" of commerce is siliceous earth more or less saturated with the liquid. These elements are not combustible, nor do they combine easily with oxygen. Indirectly oxygen forms compounds with chlorine and iodine, but none with bromine is known, although compounds of bromine, hydrogen, and oxygen are made. They readily combine with hydrogen (halogen acids) and the metals. Hydrogen and some metals burn in chlorine, as they do in oxygen. The attraction chlorine exhibits for hydrogen is so great that it will remove that element from many of its compounds; for example, under the influence of sunlight, it decomposes water: —

$$H_2O + Cl_2 \rightleftharpoons 2\ HCl + O.$$

It will be observed that but one atom of oxygen in the molecule is indicated. This is supposed to be the case for the instant, but not for any length of time, as the final oxygen obtained shows two atoms in the molecule. When an element is had thus temporarily in the free or *nascent* condition, it is more active than when it exists as the normal molecule. Colored cloth exposed to ordinary oxygen is not affected. It is bleached by nascent oxygen. Chlorine destroys many colors. The bleaching action is attributed to the liberation of nascent oxygen, for the objects must be wet. Concentrated water solutions of chlorine and bromine, when cooled, give crystals $Cl_2, 10\ H_2O$, and $Br_2, 10\ H_2O$. Charcoal absorbs 200 times its volume of chlorine.

For other reasons than similarity of occurrence we may consider the element fluorine at this point. It has never been found in nature as the free element, but always combined with some metal in salts, as fluorspar (calcium fluoride, CaF_2) and cryolite (aluminum sodium fluoride,

AlF_3, $3\,NaF$).* Small amounts are found in bones and the enamel of teeth.

While desirable, it is not necessary that the element is actually isolated that we may be convinced of its existence. Fluorine was known and accepted as an element for seventy-five years before it was obtained free from other elements. This Moissan accomplished (1886) by the electrolysis of anhydrous liquid hydrogen fluoride (at − 23°) in vessels made of copper, coated on the inside with copper fluoride, which is not affected by free fluorine. The electrodes were made of platinum and iridium, as other metals combine at once with fluorine. Pure hydrogen fluoride does not conduct the current, and fluorine decomposes water instantly, so a little potassium fluoride (KF) was added to facilitate the flow of electricity.

Fluorine compounds with all the accepted elements, except the helium group of gases, oxygen, chlorine, and bromine, are known. It is the most energetic of the electro-negative elements. It replaces chlorine in its compounds, as that element displaces bromine and iodine. It attacks all compounds of silicon, as glass or porcelain, except when perfectly dry. A drop of water brought in contact with fluorine is decomposed at once to produce ozone: —

$$3\,F_2 + 3\,H_2O \rightleftarrows 6\,HF + O_3.$$

Its action on organic material is extremely destructive, hence it is a dangerous substance to experiment with.

All four of these elements in the gaseous condition are irritant poisons. In the liquid condition they are corrosive poisons. An alcoholic solution of iodine is used as a counter-irritant in medicine. Chlorine and bromine are

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* This formula may be written Na_3AlF_6.

powerful disinfectants. The former is used extensively for that purpose, but the coloring agents in curtains, carpets, and so forth, are destroyed. They, chlorine especially, are used for bleaching. Under six atmospheres of pressure chlorine is converted into a yellow liquid and is transported in steel cylinders.

If they are liberated they quickly form compounds, hence they do not occur free in nature, but mainly as binary compounds with metals, as CaF_2 (calcium fluoride), NaCl (sodium chloride), $MgBr_2$ (magnesium bromide), or KI (potassium iodide). They are called *halogens*, or "salt-producers."

TABLE OF THE COMPARABLE PROPERTIES OF THE HALOGENS

Element	Fluorine	Chlorine	Bromine	Iodine
Derivation of name	fluo= to flow	χλωρός yellowish green	βῶμος a stench	ἰοειδής violet-form
Symbol	F	Cl	Br	I
Atomic weight	19.0	35.46	79.92	126.92
Discoverer	Ampere *	Scheele	Balard	Courtois
Date	1810	1774	1826	1811
Physical state †	gas	gas	liquid	solid
Appearance	colorless (nearly)	greenish yellow	red	metallic § crystals
Specific gravity	....	2.45	5.52	8.7
Boiling-point	– 187°	– 33.6°	+ 59°	+ 184.3°
Melting-point	– 223°	– 102°	– 7°	+ 114°
Specific gravity, liquid	1.31	1.33	3.18	....
Specific gravity, solid	....	....	....	4.95
Solubility in water	decomposes it	1 : 2.6 vol.	1 : 30	1 : 3600
Color with starch	none	none	yellow	blue

* Long known in compounds, as fluorides, CaF_2. Moissan first isolated the element in 1886.

† At ordinary temperature, + 20°.

§ The vapor is violet.

EXERCISES

1. How do we confirm the atomic weight of oxygen as 16?

2. Write the equation for the production of bromine from hydrogen bromide, using manganese dioxide.

3. How much potassium iodide (KI) would be needed to produce 4.3 g. iodine?

4. What three principles are illustrated in the preparation of the halogens? Write an equation for each.

5. Explain the bleaching action of chlorine.

6. Can we use the oxidation method (manganese dioxide) for the preparation of fluorine from hydrogen fluoride (HF)? If not, why not?

CHAPTER IX

HALOGEN ACIDS

THE halogens form compounds with hydrogen, HCl, HBr, HI, and HF, the comparative properties of which are seen in the table. They are all colorless gases, with penetrating and suffocating odors, poisonous, neither combustible nor supporters of combustion, but extremely soluble in water. These solutions are called acids, and are corrosive. Their attraction for water is shown by fuming in the air, the moisture of which absorbs them. They cannot be collected over water. The gases and their water solutions possess strong attraction for metals and their compounds, hence are not found free in nature. Hydrogen chloride, however, occurs in certain volcanic gases and the waters flowing from the neighborhood of these volcanoes, but as it combines readily with other substances, it does not remain free long. Hydrogen chloride also exists (0.08 per cent) in loose combination with certain complicated compounds in the gastric juice, where it plays an important part in the processes of digestion.

Basil Valentine, in the fifteenth century, first produced hydrogen chloride, called at different times *marine* or *muriatic acid*, by heating a mixture of ferrous sulphate and sodium chloride. Priestley, in 1772, isolated the gas, and Davy, in 1810, proved that it did not contain oxygen.

Hydrogen chloride is called hydrochloric acid when dissolved in water. It may be prepared by the direct union of the elements: $H_2 + Cl_2 \rightarrow 2\ HCl$. These gases may be safely mixed in the dark, but a violent explosion results when the mixture is exposed to heat or bright light. Such mixtures are usually prepared only for demonstration purposes, and must be avoided in the laboratory. Hydrogen burns quietly in an atmosphere of chlorine, and chlorine burns in hydrogen. Hydrogen chloride is produced in either event. This fact has recently been applied technically with success.

The usual method followed depends upon the interaction of sodium chloride (salt) and sulphuric acid (oil of vitriol):

$$NaCl + H_2SO_4 \rightleftarrows NaHSO_4 + \uparrow HCl.$$

As sodium chloride is much cheaper than hydrogen chloride, the hydrogen chloride is generated by the above reaction in the apparatus in the preparation of chlorine by the manganese dioxide method:—

$$2NaCl + MnO_2 + 2H_2SO_4 \rightleftarrows Na_2SO_4 + MnSO_4 + 2H_2O + Cl_2.$$

Hydrogen chloride has a specific gravity of 1.26. One liter of hydrogen chloride weighs 1.63 g. These figures are experimentally determined or may be derived from data already given. One liter of hydrogen weighs 0.0899 g. and one of chlorine, 3.167 g. The sum of these, 3.256 g., divided by 2, as two volumes of hydrogen chloride are obtained, gives 1.6284 +. It is not always easy to keep in mind a large variety of values, such as these figures (see table), and in fact often it is not necessary. By knowing a few values and applying one or two principles the figures for any gas may be quickly derived. For example, first, suppose we want the figure representing the specific gravity of, say, chlorine. We have learned that the specific gravity of hydrogen is 0.069 +, hence it is 14.4 times lighter than air. These facts must be remembered. As each molecule of hydrogen contains two atoms, then any volume of air weighs 28.8 + times as much as a corresponding volume of free hydrogen atoms. As chlorine has two atoms in the molecule, the molecular weight is $35.45 \times 2 = 70.9$. If this is divided by 28.8 +, we get 2.45 as the value desired. Second, suppose we want the figure representing the *weight of a liter* of a gas. The weight of a liter of air is 1.29 + g., the third fact to be remembered. The figure obtained by the first procedure, that is, the specific gravity, is multiplied by 1.29; in this case, $2.45 \times 1.29 = 3.16$ g. for the weight of a liter of chlorine. These data presuppose a knowledge of the molecular weight. Third, in case we have a gas whose *molecular weight* is unknown, we may derive it by experimentally determining the weight of a liter and reversing the calculation. Divide that value by 1.29 + and we secure the specific gravity, which, multiplied by 28.8 +, gives the molecular weight. For chlorine we secure the figure 70.76. As the atomic weight of chlorine is 35.45, we know the molecule contains two chlorine atoms.

One part of water at + 15° dissolves 450 times its volume and at 0° 505 times its volume of hydrogen chloride, giving the concentrated acid. The dilute acid contains 10 per cent of hydrogen chloride. The solution is a strong acid which dissolves many metals, oxides, and carbonates. At − 22° crystals of $HCl, 2\,H_2O$ separate out. At 110° a liquid containing 20.24 per cent distills over, which indicates some form of union between HCl and a definite amount of water, $HCl, 8\,H_2O$.

Hydrogen Bromide, HBr, Hydrobromic Acid.

Hydrogen and bromine also combine when heated together. Hydrogen bromide is not prepared pure by the action of sulphuric acid on sodium bromide, as hydrogen chloride is obtained from sodium chloride, for the strong sulphuric acid brings about decomposition with the production of free bromine. This is probably due to a weaker attraction between hydrogen and bromine than exists between hydrogen and chlorine.

It is prepared by using another and weaker acid, as phosphoric:—

$$(a)\ 2\,NaBr + H_3PO_4 \xrightarrow{} Na_2HPO_4 + \uparrow 2\,HBr,$$

or more usually by the action of water upon phosphorus tribromide:—

$$PBr_3 + 3\,H_2O \xrightarrow{} P(OH)_3 + \uparrow 3\,HBr.$$

In practice the bromide is made in the same apparatus. Then we have this reaction:—

$$(b)\ P + 3\,Br + 3\,H_2O \xrightarrow{} P(OH)_3 + \uparrow 3\,HBr.$$

An 82 per cent solution may be had which has a specific gravity of 1.78.

Hydrogen Iodide, HI, Hydriodic Acid.

Hydrogen and iodine do not combine when brought together, except on careful and gentle heating. The reaction is endothermic. Such compounds are readily decomposed, as they are in unstable equilibrium. This one breaks up easily into hydrogen and iodine, and has the power of removing oxygen from other substances, as the hydrogen is liberated in the nascent state. It will be observed that the stability of these compounds decreases with the increase in molecular weight.

Hydrogen iodide is prepared according to equation (*b*) given for hydrogen bromide, by substituting iodine for bromine.

Hydrogen Fluoride, H_2F_2 or HF, Hydrofluoric Acid.

While resembling the other halogen hydrides in many respects, hydrogen fluoride differs in several ways. The pure compound is made by heating hydrogen potassium fluoride: —

$$2\,HKF_2 \xrightarrow{} 2\,KF + \uparrow H_2F_2.$$

For ordinary purposes, however, calcium fluoride is treated with sulphuric acid. This preparation contains water from the acid used.

$$CaF_2 + H_2SO_4 \xrightarrow{} CaSO_4 + \uparrow H_2F_2.$$

It is a colorless liquid below + 19°. Above that it is a colorless gas with a very irritating odor. Below + 40° it has the formula H_2F_2, whereas above + 88° it is HF.

The utmost care must be exercised in handling this acid. A drop upon the hand, especially under the finger nail, produces a mean sore, sometimes requiring months to heal. It attacks many substances vigorously, especially when any silicon compound, as quartz, is present. When free from water, it does not attack these substances. The water solutions are kept in platinum, caoutchouc, or ceresine vessels. It is used for etching glass. It is produced in large quantities, but diluted, in the manufacture of phosphatic fertilizers. If it is allowed to escape freely in the air, serious injury to plants and animals is liable to result.

Acids. These halogen compounds all admit of hydrogen being readily replaced by more strongly electropositive elements, as the metals. They are known as acids; in this particular case, halogen acids. In acids the negative characteristic of the whole compound predominates. Acids, as a rule, are sour when soluble. They change vegetable colors, and form salts.

HALOGEN ACIDS

Name	Hydrogen Fluoride	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Iodide
Symbol . . .	H_2F_2 (above + 88°, HF)	HCl	HBr	HI
Molecular weight	40 (or 20)	36.46	81	128*
Ordinary name in water solution .	Hydrofluoric acid	Hydrochloric (muriatic) acid	Hydrobromic acid	Hydriodic acid
Physical state . .	gas (liquid below + 19°)	gas	gas	gas
Specific gravity .	0.69 (below + 19° = 0.98)	1.26	2.79	4.4
Boiling-point . .	+ 19°	− 83°	− 73°	− 34°†
Melting-point . .	− 92.5°	− 116°	− 87°	− 51°
Solubility in water	35.3%	42%	49%	57%
Specific gravity of solution . . .	1.15	1.21	1.49	1.70
Heat of formation	38.6 Cal.	22 Cal.	8.4 Cal.	− 6 Cal.
Dissociates at .	. . . .	+ 1500°	+ 800°	+ 180°

* Round figures used.

† Under four atmospheres pressure.

EXERCISES

1. Why was it necessary to prove that hydrogen chloride contained no oxygen?

2. How much salt is necessary to produce 480 g. of chlorine, and how much space would be filled by that amount of chlorine at 20° C. and 755 mm. pressure?

3. The specific gravity of hydrogen iodide is 4.4. Calculate its molecular weight.

CHAPTER X

THE ALKALI METALS

Combined with the halogens in sea water are several metals, but two in particular, sodium and potassium, appropriately claim attention at this point. Compounds of these metals have been known and used since very early times. The Israelites used a mineral-alkali (natrona,—natural sodium carbonate) for washing purposes. For a long time these caustic alkalies were regarded as undecomposable. Just a century ago, Davy, by the use of the electric current, and Gay-Lussac and Thénard, by heating the caustic alkalies with iron filings, obtained brilliantly lustrous, crystalline metals which decompose water, re-forming the fixed caustic alkalies.

Sodium is found in many silicates (oligoclase, $NaAlSi_3O_8$, with some Ca, and labradorite, $CaAl_2Si_2O_8$, with some Na), sulphates, carbonates, borates, fluorides (cryolite), and so forth, but chiefly as sodium chloride, or common salt, in the sea and as rock salt.

Potassium is a constituent of certain silicates, as mica and feldspar (orthoclase, potassium feldspar, $KAlSi_3O_8$; albite, soda feldspar, $NaAlSi_3O_8$), and occurs as salts, frequently accompanying sodium. It is found in the ashes of plants, of which it is a necessary constituent. Formerly most of it was obtained from wood ashes; now it comes mainly from the Stassfurt salt beds of Germany.

The year after Arfvedson discovered lithium, so named by Berzelius because he thought it was to be found only in minerals, Gmelin (1818) observed that its salts gave a red coloration to an alcohol flame. Lithium is a constituent of some silicates (lithia mica), soils, plants (as tobacco and beet roots), and waters. It occurs very widely distributed, but in exceedingly small amounts.

Rubidium constitutes 0.5 per cent of the mineral lepidolite. It is present to the extent of 0.025 per cent in carnallite ($KCl,MgCl_2,6H_2O$), one of the important Stassfurt salts. About 1,500,000 tons of potassium salts are mined at Stassfurt yearly. Some 300 tons of rubidium are annually distributed, mostly with fertilizers. Rubidium salts, which occur in saline waters, give two red and two violet lines in the spectrum, which are characteristic.

Cæsium is found in the mineral pollucite (cæsium aluminum silicate), and was discovered in the mother liquors obtained by evaporating large quantities of saline water. Its salts give two characteristic lines in the blue portion of the spectrum. Cæsium was the first metal to be discovered by means of the spectroscope, which instrument has made our knowledge of this and other worlds vastly broader.

These five metals may be prepared: —

First, by passing a direct electric current through the fused compounds, as NaOH.

Second, by electrolysis of a halide in a proper liquid, as pyridine, in this particular case: —

$$2\,LiCl \rightleftarrows 2\,Li + \uparrow Cl_2.$$

Third, by heating a carbonate with carbon or iron carbide: —

$$K_2CO_3 + 2\,C \rightleftarrows 2\,K + \uparrow 3\,CO.$$

All have a bright, lustrous, metallic appearance when freshly cut; all are soft and have low melting-points.

Lithium is the lightest of all the elements that are solid at the ordinary temperature. It floats upon naphtha.

They are all intensely electro-positive and hence have powerful attraction for electro-negative elements, like oxygen and the halogens. They decompose water at ordinary temperatures, evolving hydrogen and forming hydroxides: —

$$2\,Na + 2\,H_2O \xrightarrow{} 2\,NaOH + \uparrow H_2;$$

hence, they must be kept in petroleum or one of its products. In decomposing water by means of potassium, the hydrogen takes fire at once, the flame having a purple color. Sodium must be confined to take fire. It gives a yellow color to the flame.

They form alloys with certain metals, as lead, giving "hydrone," which reacts with water as above. The lead serves as a convenient medium for diluting the sodium and a safer means for its transportation. They form amalgams with mercury, being dissolved by the quicksilver.

The hydroxides formed by the action of the alkali metals on water are all soluble in water and cause litmus to assume a blue color. They are known as *bases*. If we
write the formula for water in this manner, $H-OH$,
and the formulas of the hydroxides underneath, $Li-OH$
it appears that a base may be defined as water $Na-OH$
in which one hydrogen atom has been replaced $K-OH$
by an electro-positive element. It will be ob- $Rb-OH$
served that two elements (OH) persist in these $Cs-OH$
compounds together. They constitute an electro-negative group, as it were. It is known as *hydroxyl* and is present in a large number of compounds. There are insoluble bases known. Those soluble in water as a rule change vegetable colors.

PROPERTIES OF THE ALKALI METALS

Name	LITHIUM	SODIUM	POTASSIUM	RUBIDIUM	CÆSIUM
Derivation . .	λίθος . (stone)	(natrium) soda (natrona)	(kalium) potash (alkali)	rubidus (dark red)	cæsius (blue-gray)
Symbol . . .	Li	Na	K	Rb	Cs
Discoverer . .	Arfvedson	Duhamel du Monceau and Marggraf	Duhamel du Monceau and Marggraf	Bunsen and Kirchhoff	Bunsen and Kirchhoff
Date	1817	1732 and 1759[*]	1732 and 1759[*]	1861	1860
Atomic weight .	7.00	23.00	39.10	85.45	132.81
Specific gravity	0.59	0.98	0.87	1.52	1.85
Melting-point .	+ 180°	+ 95.6°	+ 62°	+ 38.5°	+ 26.5°
Boiling-point .	> 950°	+ 742°	+ 667°	. . . .	+ 270°
Alcohol flame colored . .	red	yellow	gray-purple	dark red	blue-gray

If we again write the formula for water, and the formulas of the halogen acids beneath, we get —

$$\begin{array}{l} H - OH, \\ H - Cl \\ H - Br \\ H - I \end{array}$$

Therefore it appears that an *acid* is water in which the hydroxyl has been replaced by an electro-negative element. We know of no acid without a replaceable hydrogen atom.

If we bring an acid and a base together,

$$NaOH + HCl \rightarrow H_2O + NaCl,$$

water is eliminated and a *salt* is produced. *Neutralization* has taken place. We determine the *neutral point* by adding

---

[*] Compounds of these metals have been known since ancient times. The *savants* named first showed the distinction between soda-ash and pot-ashes. In 1807, Humphry Davy first obtained the elements by electrolyzing the fused alkalies.

a few drops of a litmus solution. The acid turns this red, the base blue. At the point when just a drop of either solution of acid or base causes the liquid to assume one color or the other, it is said to be *neutralized.* Elaboration of these terms will become necessary later, but what is given above will answer our present requirements.

Application of the principle of neutralization gives us a means for quantitative analysis, for a definite amount of a base requires a definite amount of acid to neutralize it. If we have 2 g. of NaOH, for example, dissolved in water, we need 1.825 g. HCl with which to neutralize it. This figure is derived from the molecular proportions: —

$$\mathrm{NaOH} : \mathrm{HCl}$$

$$40 : 36.5 :: 2 : x = 1.825.$$

The amount of water present as the solvent is immaterial as far as the reaction is concerned, but of importance in determining the strengths of the solutions involved. For instance, the 1.825 g. HCl may be in 100 or 1000 cc. By dividing the weight of the solute by the volume of the solvent we get the strength. In this manner we are able to determine the strength of an unknown solution. Once the strength of a solution becomes known, it becomes a *standard solution.* If the solution contains in 1000 cc. the number of grams equal to the molecular weight of the solute, it is called a *molar solution.* For example, 40 g. of NaOH and 36.5 g. HCl each in 1000 cc. are molar solutions. One cubic centimeter of one such solution neutralizes 1 cc. of the other. Another term, *normal solution,* is also applied to such solutions, but it does not always mean the same thing. Sulphuric acid (H_2SO_4), for instance, has two hydrogen atoms, which may be replaced by a metal; therefore, it has a double equivalence. Normal solutions refer to this equivalence.

A molar solution of sulphuric acid contains 98 g. to the liter ($2 + 32 + 64 = 98$), whereas the normal solution contains one half (49 g.) that amount. In the case of the HCl, the normal and the molar solutions are the same. A standard solution containing one half, one tenth, or other fraction (x) of a normal or molar strength is indicated by symbols in this manner: $\frac{N}{2}$, $\frac{N}{10}$, $\frac{N}{x}$, or $\frac{M}{2}$, $\frac{M}{10}$, $\frac{M}{x}$, and so forth. A multiple molar or normal solution is indicated by the integer being placed in front, as, 2 M, 5 M, or 3 N, 5 N, and so forth.

The use of solutions in analysis in this manner is known technically as *acidimetry* or *alkalimetry*.

EXERCISES

1. Compare the specific gravities, melting and boiling points, of the alkali metals, and see if any relationship appears with the atomic weights.

2. Explain the relationship of an acid, a base, and a salt.

3. How much of the following substances are in their molar solutions: hydrogen bromide, potassium hydroxide (KOH), and potassium iodide (KI)?

4. Suppose we have a molar solution of sodium hydroxide and a hydrogen chloride solution of unknown strength. If 50 cc. of the former require 62 cc. of the latter for neutralization, what is the strength of the hydrochloric acid solution?

CHAPTER XI

NITROGEN — AMMONIA — LIQUEFACTION OF GASES — COMPOUND RADICALS

NITROGEN, N. At. Wt., 14.01. M. Wt., 28.02, N_2

IN 1772 Rutherford discovered that part of the air did not support respiration or allow combustion. It was called "mephitic" or "phlogisticated air." Lavoisier called it *azote* (devoid of life). Chaptal gave it the English name nitrogen, indicating a producer of niter or saltpeter (KNO_3).

In the free state it constitutes four fifths by volume or three fourths by weight of the air. It is combined with oxygen in nitric acid and in the nitrates; with hydrogen in ammonia and its compounds. Nitrogen is an invariable constituent of protoplasm and many animal and vegetable substances. No living matter is known free from nitrogen compounds.

It is prepared, but in an impure form, by the removal of oxygen from the air; either

(*a*) By burning phosphorus in the air; or,

(*b*) By the absorption of the oxygen of the air by an alkaline pyrogallate.

It is prepared pure by heating ammonium nitrite:

$$NH_4NO_2 \rightarrow 2\,H_2O + \uparrow N_2.$$

It is a colorless, odorless, tasteless gas, with sp. gr. 0.97, b.-p. — 193°, freezing-point — 203°. The specific gravity of the solid at — 214° is 0.885. One liter weighs 1.2507 g. Water dissolves 0.015 volume at ordinary temperatures.

Nitrogen is a very inert element, combining directly only with lithium at ordinary temperatures (Li_3N), and a few other metals, as magnesium (Mg_3N_2), when heated. Under the influence of sparks from high-tension electric currents it combines with oxygen. Indirectly it combines with many of the elements, giving important ammonium and nitric acid compounds, explosives, alkaloids, and albumenoid substances. Decay usually starts in the last-mentioned compounds of nitrogen. It is not itself a poisonous element, but many of its compounds are.

It serves not only to dilute the oxygen of the air, and thus prevent combustion processes once inaugurated from bringing about a rapid destruction of our living world, but is an essential constituent of plant food. Free nitrogen is not a direct food for vegetation. It must be in the form of compounds like ammonia, or nitrates, or the many complicated compounds we find produced in the growth and decay of living things. There are certain plants, like peas, beans, clover, and so forth (*leguminosæ*), which have nodules upon their roots. These nodules contain bacteria which have the power of converting free nitrogen into compounds, chiefly albumins. These bodies are digested and absorbed by the roots of the plant. Some of the nodules often contain as much as 5 per cent of combined nitrogen. The roots of such plants are not harvested, but are plowed into the soil, thus enriching it. Nitrogen compounds that are usually applied as fertilizers, are soluble in water, or readily undergo decomposition (nitrification and denitrification), forming the soluble compounds, hence are washed out of the soil. Nitrogen is therefore the most expensive of the essential elements for plant growth. The discovery of the ability of the leguminosæ to utilize the free and abundant nitrogen of the air constituted one of the greatest contributions to agronomy.

AMMONIA, NH_3. M. Wt., 17.03

Of the compounds of nitrogen and hydrogen we need give attention here to but one, namely, *ammonia*, which was called "alkaline air" by Priestley, who discovered it (in 1774). In 1785 Berthollet proved its composition.

It occurs in very small amounts in the air and rain in compounds, as the carbonates, nitrates, and nitrites. It results from the decay of nitrogenous organic matter (denitrification). Ammoniacal salts are found in plant and animal matter, especially in decomposed urine.

Four processes for the preparation of ammonia may be considered, as they separately illustrate principles: —

1. Nitrogen and hydrogen can be made to combine under the influence of a silent electric discharge:

$$N_2 + 3\,H_2 \rightleftarrows 2\,NH_3;$$

but the yield is small. It is a reversible reaction.

2. Decomposition of a metallic nitride with water:

$$Mg_3N_2 + 3\,H_2O \rightarrow 3\,MgO + \uparrow 2\,NH_3.$$

3. Decomposition of a compound of ammonia itself: (*a*) by heating ammonium hydroxide,

$$NH_4OH \leftrightarrows \uparrow NH_3 + H_2O;$$

(*b*) by contact, or heat, with a metallic oxide (calcium oxide),

$$2\,NH_4Cl + CaO \rightarrow CaCl_2 + H_2O + \uparrow 2\,NH_3.$$

4. By breaking up complicated compounds of nitrogen by heat; for instance, when wood, coal, animal refuse, and so forth, are heated in a retort, so arranged that the oxygen of the air is excluded. This is known as the process of *destructive distillation*, which is extensively used commer-

cially and is so complicated that no chemical equations have been devised to show exactly what takes place.

Ammonia is a colorless gas with a very pungent odor, familiarly known in smelling salts. It is lighter than air (sp. gr. 0.59). Under a pressure of 6.5 atmospheres, or when cooled to − 40° under ordinary pressure, it condenses to a colorless, mobile liquid (sp. gr. 0.623), which freezes at −85°. Its melting-point is −75° and boiling point −34°.

Liquefaction of Gases. Boyle, Northmore, van Marum, Faraday, and others, found many gases could be converted into liquids on increase of pressure, especially if the gas was simultaneously cooled. Up to 1877 hydrogen and several other gases were considered non-condensable, although Natterer (1852) had applied a pressure of over 3000 atmospheres. In 1869 Andrews discovered a principle, the ignorance of which caused previous failures; namely, that each gas has a temperature above which no amount of pressure so far attainable suffices to condense it to a liquid. This is known as the *critical temperature*, and the pressure exerted by the particular gas at that temperature is known as the *critical pressure.* Since the acquisition of this knowledge, all gases have been converted into liquids, and many into solids.

Cullen observed that when a liquid was rapidly converted into a gas, cold was produced. This principle has been applied in making ice machines. If ammonia gas is compressed, it changes into a liquid. The heat liberated is removed by cold water flowing through pipes immersed in the liquid. The cooled liquid ammonia, when run into other pipes under less pressure, evaporates and absorbs heat from any surrounding liquid, which is usually one not frozen, or only partially frozen, at the low temperature produced. This very cold liquid, usually a calcium chloride brine, is led by pipes through the localities to be cooled back to the refrigerating machine, where it is again chilled. The ammonia gas flows out through a separate system of pipes, is recondensed, and used over again. The brine and ammonia are in separate closed systems of pipes.

Pure liquid ammonia does not conduct a current of electricity. It dissolves many solids and, like water, forms crystalline compounds (ammonia of crystallization), ammoniates, similar to the hydrates.

Ammonia is exceedingly soluble in water; at $+16°$ water dissolves 739 and at $0°$ 1148 times its volume. It cannot, therefore, be collected over water, but may be over mercury or by upward displacement. The water solution is known as ammonium hydroxide, aqua ammonia, or spirits of hartshorn. The concentrated solution at $+15°$ contains 35 per cent and has a specific gravity of 0.882. When ammonium hydroxide is heated, ammonia is driven off. Care should be exercised in opening a fresh bottle of ammonium hydroxide, especially in warm weather, as the contents are often charged at low temperatures.

Ammonia is not ordinarily considered a supporter of combustion. It burns when the gas is held in a flame, but ceases to burn when not heated. It burns in oxygen, however.

Compound Radicals. Ammonia acts like an element in many ways. It is decomposed, however, when passed over certain heated metals: —

$$2\,NH_3 + 2\,K \rightarrow 2\,NH_2K + H_2.$$

Ammonia combines directly with hydrogen chloride to form ammonium chloride: —

$$NH_3 + HCl = NH_4Cl.$$

The formula for ammonium hydroxide is written NH_4OH. The (NH_4) group enters many compounds in the same manner as an element (NaCl, KCl, NH_4Cl), and forms an amalgam as sodium does, although free ammonium has not been prepared. When a combination of atoms acts like an element, we speak of the combination as a *compound radical.*

Ammonium hydroxide turns litmus paper blue, neutralizes acids, and acts like sodium hydroxide, except that in gentle heat it is decomposed, with the evolution of ammonia gas. We readily appreciate why Priestley designated it "alkaline air."

We may now enlarge our definition of a base. —

A base may be regarded as water (H – OH) *in which one hydrogen atom has been replaced by an electro-positive element or compound radical* (NaOH, KOH, NH_4OH).

EXERCISES

1. How much nitrogen may be obtained from 22 g. of ammonium nitrite? What volume would it occupy at + 20° and 756 mm. pressure?

2. What are the principles illustrated in the methods given for the preparation of ammonia?

3. What relation is there between the principles involved in the liquefaction of gases and vapor tension?

4. Why should care be exercised in opening vessels containing concentrated ammonia water?

CHAPTER XII

THE AIR AND ITS CONSTITUENTS—THE NOBLE GASES

About the ninth century chemists knew that metals were altered when calcined in the air. Jean Rey proved the materiality of air, which was confirmed by Galileo in 1640 and von Guericke, by means of the air pump, in 1648. In the seventeenth century Hooke suspected that the air contained the gas given off by heating niter. Mayow, in 1669, demonstrated that the volume of air contained in a vessel over water was diminished by respiration as well as by combustion. Becher, in 1700, thought combustion originated from a peculiar volatile substance escaping from the earth or a kind of sulphur. Stahl, his pupil, in 1720, put forward the hypothesis of "phlogiston," or "burnableness," which he said was the substance that escaped in combustion. Rutherford, in 1772, discovered nitrogen, and Bayen, in 1774, showed that mercuric oxide was reduced without the addition of phlogiston. These led Lavoisier to his experiments on the absorption of air by the calcination of metals and to his demonstration of the law of the conservation of matter. A century later Rayleigh and Ramsay proved the presence of argon.

The exact thickness of the gas envelope surrounding the earth, called the atmosphere, is not known. It is essentially a mixture of nitrogen, oxygen, and argon (including the so-called "noble gases"), with a certain more or less constant admixture of carbon dioxide and variable amounts of aqueous vapor and oxygen, nitrogen and hydrogen compounds. There are also found fortuitous substances, like dust, sulphur dioxide, and so forth, depending upon the locality, time, and conditions.

The air is not constant in its composition. Certain constituents vary but slightly, however, from a definite percentage. The air over the sea, upon mountain tops, in deep mines, and in cities appears to be different, and does differ in detail, but the average analysis of samples of air collected the world over, eliminating all but the first three constituents mentioned, shows the following composition :—

	Per Cent by Volume	Per Cent by Weight
Nitrogen	78.06	75.5
Oxygen	21.00	23.2
Argon	0.94	1.3

In making the analysis a definite volume of air is first treated with yellow phosphorus in wire form. This quickly combines with the oxygen, the amount of which is determined by the shrinkage in volume. The remaining gas is then passed over heated magnesium, which combines with the nitrogen (Mg_3N_2). That which is not removed is argon.

The air is not a compound, because (1) the constituents are not present in atomic proportions; (2) when the elements composing air are mixed to form air, there is neither an absorption nor an evolution of heat, which would indicate chemical combination; and (3) the constituents of the air vary in their solubility in water. Air, expelled from water, contains 34.9 per cent of oxygen and 65.1 per cent of nitrogen.

One liter of air weighs 1.29276 g. Air is 773 times lighter than water. It is 14.39 times heavier than hydrogen. By application of the principles governing the liquefaction of gases, namely, with slight pressure and intense cooling, it is converted into a colorless liquid (Processes of Hampson and Linde), with boiling-point −190°, specific gravity 0.995. It is usually turbid, due to the presence of solid carbon dioxide in suspension. Nitrogen boils at −193° and oxygen at −184°; consequently, after standing, much of the nitrogen boils off, and the liquid air contains about 54 per cent of oxygen instead of 23 per cent. With care the percentage of oxygen may be increased to 90 or even 95. By its evaporation, great cold is produced. The properties of many substances are altered by this intense cold. Rubber loses its elasticity and becomes hard and brittle. Flowers dipped into liquid air are easily shattered into minute fragments by the least pressure. Chemical reactions are especially slow, some violent ones scarcely proceeding at the temperature of −193°. Experiments with liquid air on a large scale and modern cryogenic investigations were made possible by the use of glass vessels of double walls separated by a vacuum. Dewar perfected these by silvering the walls of the evacuated space to reduce the heating effect of transmitted light.

THE NOBLE GASES

In 1892 Rayleigh noted that while a liter of nitrogen obtained from the air weighed 1.2571 g., a liter of the pure gas weighed 1.2507 g. He and Ramsay then separated from the air a new element, called argon, by the method given above. It received its name on account of its chemical inactivity. We inhale about 20 l. of this gas every day. As far as we are aware, it is devoid of physiological action. One hundred volumes of water dissolve 4 volumes of argon at +12°; hence it is found in rain-water. Argon is therefore present in many waters, and the gases from springs, as well as in certain minerals like cleveite, uraninite, and malacone. It has been found in meteorites, and the gases contained in rock salt. It boils at – 185°, and forms ice-like crystals at – 189.5°.

In 1868 Jannsen and Lockyer observed lines in the chromosphere of the sun which could not be attributed to any known chemical element, and helium was prognosticated. In looking for richer sources of argon, Ramsay found these lines in gases obtained from certain minerals. It is a very inert gas. One hundred volumes of water at + 18° dissolve 0.73 volume of helium. This gas resisted liquefaction longer than any other. As these pages pass through the press, Onnes, in Leyden, announces that he has liquefied it, and that it boils at – 268.5°. Ramsay and Travers, after fractioning large quantities of liquid air, also separated out neon, krypton, and xenon. These occur in extremely small amounts in the air.

Derivation of Names	Atomic Weight	One Part by Volume in Air
Helium — *ἥλιος* — sun	4.0	2,450 vols.
Neon — *νέος* — new	20.	808 vols.
Argon — *ἄργος* — idle	39 9	105 vols.
Krypton — *κρυπτός* — concealed	81.8	746,000 vols.
Xenon — *ξένος* — stranger	128.0	3,846,000 vols.

The experimental difficulties attendant on investigations at such low temperatures as were necessary in the discovery and study of these gases, were very great. We can picture the difficulties to be encountered in working with ordinary substances, if all the apparatus is at the temperature of boiling oil of vitriol (+ 270°). These difficulties were surmounted by the experimental ingenuity of Dewar, Ramsay, Olszewski, and Onnes, for ordinary zero is that much higher than the lowest temperature so far attained.

These gases have one atom in the molecule (monatomic). They are more inert than nitrogen. No compounds have been prepared which give evidence of the union of any of these five elements with other elements or even with each other. They are therefore called "noble gases." Under certain conditions different ones are obtained from radioactive compounds (Chapter XXV).

Carbon dioxide (CO_2) is a constant constituent of the air, averaging about 3.5 parts per 10,000. On high mountains the figure falls to 2 parts, while it is much higher at other places. Inspired air containing 3 parts is expired with 400 parts of carbon dioxide per 10,000. The percentage of oxygen drops from 21 to 17, or lower. An inhabited room with ordinary ventilation contains 6 to 7, and with poor ventilation 30 and more parts of carbon dioxide per 10,000.

The carbon dioxide in the air comes mainly from the oxidation of organic matter (vegetable, animal, and mineral), either by combustion, or respiration, or from decomposition. Estimating the population of the globe at one and a half billions, mankind alone exhales one and a half million tons of carbon dioxide every day. In the city of New York about 100,000 tons of carbon dioxide are daily poured into the air from the combustion of fuel. We have an uninterrupted and constant production of carbon dioxide through the decay of vegetable matter. Large quantities come from mineral springs and volcanoes. Carbon dioxide is heavier than the air and accumulates in some low places, as wells, fermenting rooms of breweries, and some valleys. Through the agency of the winds, rains, and the ceaseless movement of the molecules (diffusion), it is distributed in the atmosphere. This is very fortunate. A candle ceases to burn when the percentage of oxygen gets below 18. To avoid danger from vitiation of the air, it has become generally recognized that from 16 to 20 cubic meters of air are required per individual per hour. In the best ventilated hospitals about 100 cubic meters are provided. Under normal conditions of health half that amount is sufficient. As a general rule, the atmosphere of a room may be considered vitiated as soon as it begins to "smell close." This condition is not all due to carbon dioxide, however, but to organic substances, only partly known, which are exhaled by man and animals, probably as much from the skin as from the lungs. We have no simple method for estimating these organic substances. They may be regarded as roughly proportional to the carbon dioxide, so a safe criterion in judging the quality of the air is the determination of the amount of carbon dioxide present. This may easily be done by its conduct with clear lime-water, which, on coming into contact with carbon dioxide, becomes turbid: —

$$\mathrm{Ca(OH)_2 + CO_2 \rightarrow \downarrow CaCO_3{}^{*} + H_2O.}$$

Aqueous vapor is always present. Its quantity depends upon the temperature and corresponds to the vapor tension of water. One cubic meter of air saturated can contain 22.5 g. of water at + 25°. On cooling to 0°, 17.1 g. separate out. It has been estimated that there are 72×10^{16} tons of water in the air. Aqueous vapor is very unequally diffused. Generally air contains from 50 to 70 per cent of the quantity of vapor necessary for complete saturation. The amount of vapor in the air may remain the same, while the temperature varies and it feels "too dry" or "too

* The arrow pointing down indicates formation of a precipitate.

wet." The air, when dry, irritates the respiratory organs; when too moist, it impedes transpiration and its beneficent effects. The total amount of water present, therefore, plays a less important part than its relation to the temperature.

The other constant constituents in the air, but in very variable amounts, are ozone, hydrogen dioxide, and nitrogen compounds, as ammonium carbonate, nitrite, and nitrate. They are supposed to be produced through electrical and light influences, and are swept to the ground by the precipitation of aqueous vapor.

There are many incidental impurities in the air that are local and more or less evanescent. In the combustion of coal, sulphur is burned to sulphur dioxide. In the city of New York over a thousand tons of sulphuric acid from this source are poured into the air every day. The city of Manchester, England, looks like a forest of chimneys, the black smoke (soot) constituting the foliage. Finely divided particles of solids (soot, clay, sand, refuse of all kinds, and so forth) are whipped up by the winds to give us dust. Aside from general objections to personal discomfort from flying particles of solid material, whatever be its nature, there is a specific one. These particles are the bearers of germs, many of which are pathogenic. When these germs come into contact with material suitable for food and conditions favorable to growth, they develop with tremendous rapidity. Processes of fermentation, decay, and disease are thus inaugurated. Air free from solid particles is free from bacteria. We may rid the air of them by passing it through 30 to 40 cm. of cotton.

EXERCISES

1. What is the principle underlying the construction and use of Dewar flasks?

2. How many cubic feet of air are taken into the lungs (average) every hour, and how many cubic feet should be supplied per person in a well-ventilated room?

3. How would you account for the fair degree of uniformity in the mixture of gases constituting the air?

4. Why do we say air is a mixture?

5. From the following data calculate the weight in kilograms of each constituent of the air in a room 12′ × 15′ × 9′. Assume water vapor 0.90 per cent, and carbon dioxide 0.03 per cent.

CHAPTER XIII

CARBON

At. Wt., 12

THE element carbon and its compounds constitute the backbone of living things. It occurs in nature as: —

1. *Diamond*, in alluvial rocks of volcanic origin in India, Borneo, Brazil, and South Africa and in certain meteoric stones. It crystallizes in the regular system, mostly rhombic dodecahedra, occasionally as octahedra. It may be colorless, transparent, black, or varicolored, depending upon the impurities present. When diamonds are found, they are covered, as a rule, with a crust and possess none of the brilliancy we ordinarily associate with them. Pure diamonds have high dispersive and refractive powers for light. The best diamonds are the hardest known substances. Some are softer than others, and have a grained structure, which is observed in the cutting. On account of the hardness, the black, impure form, bort, is used extensively in diamond drills for cutting and boring. The better grade is cut and polished into shapes, which must not be mistaken for the underlying crystalline form, to produce the greatest luster and brilliancy, and used for gems. Diamonds are sold by the "carat," equal to $3\frac{1}{6}$ Troy grains or 205 milligrams. One of the largest diamonds ever found, the *Cullinan*, weighed 621 grams, or about 3025 carats.

The diamond has a specific gravity of 3.5 and is the densest form of carbon. It softens under intense heat ($+2500°$), changing into the graphitic form of carbon. When heated to + 800° in the presence of oxygen, it burns to CO_2 (in 1694 by Averami and Targioni). The diamond is one of the most insoluble substances known. Carbon in general is very insoluble, but it does dissolve in some molten metals, as iron and melted olivine (magnesium silicate), from which it may be crystallized on cooling under great pressure. Moissan prepared small synthetic * diamonds by the former process. He dissolved pure sugar charcoal in molten pure iron and suddenly cooled the very hot mass by plunging it into water. A hard exterior was thus produced. As the interior, which remained liquid, solidified, the iron carbide (Fe_3C) crystallized with expansion and consequent production of great pressure upon any uncombined carbon within the iron ball. On dissolving the iron afterwards in acids, tiny crystals of diamonds were found. Carbon, and a few other substances, on being heated, change into vapor before reaching the boiling-point. The critical temperature of carbon is +5800°. Its critical pressure is 17 atmospheres. By exploding some of the very high explosives in steel bombs, strong enough to withstand enormous pressures, carbon has been had in the liquid form, and as it cooled, diamonds were produced (Abel, Noble, Crookes). In no cases have diamonds so far been produced synthetically of commercial size or in quantity. Greek writers mentioned diamonds 300 B.C.

2. *Graphite* was known to the ancients, but was not distinguished until 1565 (Gesner). It occurs as an amorphous,

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* To synthesize an element seems a contradictory term. In this case it is not. We know diamond is the densest form of carbon, and we have reason to believe it has the largest number of atoms in the molecule of any form of carbon. Therefore the term means an increase or building up of a larger, heavier, or more complex molecule. "Artificial" diamonds are made of glass and contain no carbon and do not possess the properties of diamonds, while "synthetic" diamonds do.

grayish black, glistening, soft mass and as rhombic prisms and hexagonal plates in old rock formations in Siberia, Ceylon, and the United States. It is frequently called plumbago, or black lead, and is used in making lead pencils and stove polish. It has a specific gravity of 2.25. It is a good conductor of heat and electricity, hence is extensively used in making crucibles, in electroplating, and as electrodes, where heavy currents are used and substances like chlorine, sodium, phosphorus, or the alkaline hydroxides, which attack metallic electrodes, are produced. It is attacked by some powerful oxidizing agents. It may be burned by heating in oxygen, but this occurs at a higher temperature than the diamond requires. It appears to be the stable variety of carbon, as other forms of carbon when heated pass into it. This is accomplished by fusing other forms of carbon with iron, but it is produced commercially in large quantities by heating carbon to a high temperature, but below +4000°, by means of an alternating electric current. It has an "oily feel" and is used as a lubricant where an oil would be decomposed by the heat or squeezed out by the weight of the machinery. Recently Acheson has also prepared graphite in such a fine state of subdivision that it remains suspended in water for months and readily passes through filters.

3. *Amorphous carbon* is a term applied to a class to which belong the various grades of mummified and carbonized remnants of ancient flora. They vary in their purity and have an average specific gravity of 1.5. The natural varieties are peat, lignite, bituminous and anthracite coal. The artificial varieties are coke, charcoal, gas-carbon, soot, lampblack, and animal charcoal.

Each of these has specific properties and uses. All of the former and the first two of the latter group are used for fuel purposes and in metallurgical processes to reduce oxides to the metallic condition and to produce carbides. They contain ash, varying in percentage from 1 to 80. Charcoal absorbs many times its volume of various gases, for which reason it is often used for deodorizing and disinfecting. When cooled by liquid air or hydrogen, this capacity is so increased that a vessel containing a gas may be brought to such a low vacuum as to prevent the passage of high-tension currents of electricity. Animal charcoal, containing about 75 per cent of bone ash, furthermore absorbs coloring matter from many liquids, so is used in decolorizing sugar solutions before the white product is crystallized out. Coke and charcoal, common and animal, are made by the destructive distillation of coal, wood, and animal refuse, respectively. Gas carbon is produced with the first and is used in electrical work. Soot and lampblack are produced by the incomplete combustion of carbonaceous material. They are virtually the same, and are used in making black printer's ink and paint.

In 1773 Lavoisier showed the similar chemical nature of the allotropic forms of carbon. The purest carbon is made in the laboratory by charring sugar.

Carbon occurs combined as carbon dioxide (CO_2) in the air; in carbonates, as limestone ($CaCO_3$) and magnesite ($MgCO_3$); as compounds with hydrogen in natural gas (methane, CH_4), petroleum (heptane, C_7H_{16}, benzene, C_6H_6), and asphalt; it is present, combined with other elements, in all animal and vegetable matter.

Carbon does not readily form combinations with the metallic elements except at comparatively high temperatures, when it acts as a negative element. Many of these carbides are decomposed at +2500°. At ordinary temperatures, it does not combine with oxygen, but when heated it forms two oxides, CO and CO_2, with the production of considerable heat. It combines when red hot with sulphur to form carbon disulphide (CS_2).

EXERCISES

1. How much carbon would be necessary to reduce 9 g. of copper oxide (CuO)?

2. What principles underlie the production of diamonds from pure charcoal?

3. How much carbon dioxide and disulphide, respectively, can be produced from 4 lb. of pure charcoal?

CHAPTER XIV

CARBON HYDRIDES — FLAME — ILLUMINANTS

ALTHOUGH carbon combines directly with great reluctance, yet it forms a number of compounds, with hydrogen. Many of these hydrocarbons occur in natural gas and petroleum; many are made artificially, as in the destructive distillation of wood and coal. Their study is extensive, and forms a prominent part of one of the divisions of chemistry called Organic Chemistry. For our purposes, we need consider only two of the hydrocarbons at present.

Methane, CH_4, m. wt. 16.032, was discovered by Volta in 1778.

Methane occurs as "marsh gas," where vegetable matter undergoes slow decomposition with limited amount of oxygen present, as when organic matter decays beneath water. It occurs, also, as "fire damp" in coal mines. It is the principal constituent of natural gas drawn from deep borings in the earth, and is found in putrefactive gases expelled from the animal body.

It may be prepared (1) by decomposing a carbide (aluminum carbide) with water or acids:

$$C_3Al_4 + 12\,H_2O \rightarrow \downarrow 4\,Al(OH)_3 + \uparrow 3\,CH_4;$$

(2) by decomposing a more complicated compound of carbon (sodium acetate) by heating with a solid caustic alkali:

$$NaC_2H_3O_2 + NaOH \rightarrow Na_2CO_3 + \uparrow CH_4.$$

It is a colorless gas, with a faint odor, slightly soluble in cold water; sp. gr. 0.56; b.-p. – 164°; m.-p. – 186°. It burns with a very hot, slightly luminous flame:

$$CH_4 + 2\,O_2 \rightleftharpoons CO_2 + 2\,H_2O.$$

It forms explosive mixtures with oxygen or the air. The explosion of such a mixture is the cause of most disasters in collieries. A mixture of fine coal dust and air is also explosive. The presence of dust, even if it is non-combustible, renders the effects of the explosion more disastrous. Many miners who do not suffer greatly from the shock of the explosion are subsequently killed by the "after damp," which is a mixture of the oxides of carbon.

CH_4 is neither acidic nor basic in character. It may give up one hydrogen atom, and the CH_3 (methyl radical) becomes a positive radical, which enters into many combinations; for instance, CH_3Cl (methyl chloride), CH_3OH (methyl hydroxide), or CH_3, CH_3 (methyl methane), which is called *ethane* and is written C_2H_6. This ethane may have one hydrogen atom substituted by CH_3, also CH_3, C_2H_5 (methyl ethane, propane, C_3H_8), which in turn may be again substituted, and so on. (*Vide* Organic Chemistry.)

The phenomenon of *combustion* is dependent upon three factors: first, something to burn; second, a supporter of the combustion; and third, a kindling temperature. We have learned that oxygen burns in hydrogen, and chlorine in hydrogen, so combustion is not essentially a process of oxidation. In everyday life, however, we regard combustion as the burning of such materials as hydrogen, coal gas, charcoal, coal, oils, fats, and so forth, in the air; in fact, an accelerated oxidation. If the combustible materials, gasified, are mixed with air and set on fire, the acceleration is so great that the combustion appears to be almost instantaneous, and an explosion results. All chemical actions are rendered sluggish at very low temperatures. Oxidation by the addition of oxygen proceeds at ordinary zero, but that is warm in comparison with − 184°. Combustion requires an even greater elevation of temperature. and once begun produces heat. The temperature at which it begins is called the *kindling point*. A mixture of hydrogen and oxygen, or methane and oxygen, is harmless until the kindling point is reached. Metals conduct heat. If, therefore, a combustible mixture is kept separated by a perforated metal screen, as wire gauze, from a fire, no explosion results. Humphry Davy devised the *safety lamp*, which is used in coal mines, by the application of this principle, in response to the demands resulting from the colliery explosions in England.

If the combustible substance is a gas which burns quietly, producing heat and more or less light, a *flame* is produced. When charcoal burns in the air, we get heat from its combustion, light from the incandescent solid, but little or no flame. If we burn an oil, we get heat from its combustion, light from the heated particles of evaporated liquid, and flame. If we light a candle, we melt some of the solid and the liquid acts as an oil. This may be readily shown by placing one end of a glass tube close to the wick, inside the flame, and inclining it at a small angle from the vertical. On placing a lighted match at the upper end of the tube, a flame is produced by the burning of the volatilized oil. When we set a stream of illuminating gas on fire, we get a flame by its combustion in the air. This is a common practice. From a strictly scientific point of view it is immaterial whether we light gas in the air, or light air in gas. The important factor is the chemical reaction of one gas with another. Heat is produced at that particular place, and the flame is made up of the matter there heated. Some gases, as hydrogen and methane, give flames that are almost invisible. The energy generated practically all goes to the production of heat. If an infusible substance, like a platinum wire, Welsbach mantle,* or finely divided carbon, iron, or other dust, is brought into such a flame, it becomes *luminous*. The luminosity of the flame is not dependent so much upon the temperature as it is upon the density of the gas and the presence of solid particles, which are heated to incandescence. The presence of solid carbon in a candle or gas flame is readily shown by cooling the luminous portion by inserting a piece of cold porcelain. Soot is deposited.

Illuminating gas is made by the destructive distillation of coal, when it is a mixture of combustible hydrocarbons, which burn with a luminous flame, or by the passage of steam over heated carbon. Gas produced by the latter method, *water gas*, is made up of hydrogen and carbon monoxide. These burn with a non-luminous flame. To render it suitable for illuminating purposes it is *carburetted*, *i.e.*, gasified carbonaceous material is added, which, when decomposed in the first burning, liberates free carbon. This heated carbon gives luminosity. As this hot carbon comes in contact with air, it is burned to invisible carbon dioxide. Therefore a gas flame has three zones, the innermost one being the first burning, which liberates carbon and is non-luminous. The middle zone is luminous; and the outer one, where the combustion is completed, is non-luminous. If the pressure is such as to force the gas from the tip at such a rate as to prevent sufficient air from coming into contact with the combustible constituents to complete the oxidation, a smoky flame

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* A Welsbach mantle is essentially a web of comparatively infusible oxides of thorium (99%) and cerium (1%).

results. This is obviated at the gas works by mixing a suitable proportion of air with the gas in advance. This brings about proper combustion at the pressure the gas is delivered to the consumer.

When gas is to be burned for heating purposes, luminosity is not desired. Water gas is most suitable for heating, and it may be used to produce light, if it is burned with a Welsbach mantle. Many consumers do not use the mantle, although many million are produced annually, and two series of gas mains would be too expensive. Bunsen invented a burner, a mechanical device for mixing sufficient air with the gas previous to its burning, which brings about such complete combustion of the constituents of the gas as to make it non-luminous. By regulating the inflow of air, the flame may be caused to assume varying degrees of luminosity. The Bunsen burner was first used with gas made from coal. The principle is now universally applied.*

The blowpipe is a mechanical device for directing the flame, insuring the complete combustion of all constituents, with localization and consequent increase of heat.

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* Coal gas for house illumination was introduced in London by Murdock in 1792. By 1815 it was used in Paris, also, for street lighting. One ton of good gas coal yields about 10,000 cu. ft. of 16 candle power gas. The average composition of the four kinds of gas is shown in the following table: —

	COAL	WATER (Fuel)	WATER (Carburetted)	PINTSCH (Oil)
Candle power	17.5	....	25.0	65.0
Illuminants	5.0	....	16.6	45.0
Marsh gas (CH_4)	34.5	1.0	19.8	38.8
Hydrogen	49.0	52.0	32.1	14.6 (ethane)
Carbon monoxide	7.2	38.0	26.1	....
Carbon dioxide	1.1	6.0	3.0	....
Nitrogen	3.2	3.0	2.4	1.1

EXERCISES

1. Why do the hot coals of a wood-fire burst into flame when they are blown upon? Why is a lighted match put out by the same procedure?

2. Explain the apparently redundant expression "oxidation by the addition of oxygen."

3. Account for the brilliant light obtained when magnesium or phosphorus is burned.

4. Why does a blowpipe give a higher temperature than a Bunsen burner?

5. Explain the phenomenon of flame.

CHAPTER XV

CARBON OXIDES—VALENCE

THREE compounds of carbon and oxygen are known, viz., CO_2, CO, and C_3O_2. Each one of these presents interesting facts, and together they illustrate important principles.

Carbon dioxide, CO_2, m. wt. 44, is the first product in the combustion of coal and the final oxidation product of all compounds of carbon, especially in the processes of fermentation, decay, and respiration. It occurs in the air (about thirty tons over each acre), in volcanic gases, dissolved in most spring waters, and, rarely, in cavities of quartz crystals. In some localities it issues from the ground in large quantities, and where topographic conditions are favorable it collects in low places, as in Poison Valley in Java and the Grotta del Cane near Naples. It is found combined with many metallic oxides, forming carbonates, as limestone ($CaCO_3$), strontianite ($SrCO_3$), and siderite ($FeCO_3$).

Van Helmont (1577–1644), who was the first to characterize various gaseous substances as different from air, called carbon dioxide "gas sylvestre," the exact reason for which we do not know. Limestone (calcium carbonate, $CaCO_3$) up to 1757 was regarded a simple substance. Black determined that carbon dioxide was given off when it was heated (in making quicklime), so he called it "fixed air." As a water solution of carbon dioxide is acid in reaction, Lavoisier called it "acide carbonique." Dalton analyzed it also, as well as carbon monoxide. He observed the ratio of carbon to oxygen in the two compounds to be 1 : 2 and 1 : 1, respectively. This relationship was one of those used by Dalton in determining the law of multiple proportions.

It is prepared —

First, by burning carbon and its compounds, between + 400° and + 700°:

$$C + O_2 \rightarrow CO_2.$$

Second, by decomposing a carbonate with an acid:

$$CaCO_3 + 2\,HCl \rightarrow CaCl_2 + H_2O + \uparrow CO_2.$$

Third, in the processes of fermentation large quantities are produced, collected under pressure in steel cylinders, and used commercially.

Carbon dioxide is absorbed by the leaves of plants from the air and is carried to the leaves in solution by the juices of the plant from the water in the soil. There under the influence of light and in the presence of chlorophyl, the coloring matter of the leaves, it is converted into more complicated carbon compounds, and oxygen is liberated through the stomata. An acre of oats liberates about the same amount of oxygen as it absorbs carbon dioxide in the growth and maturing of the plants.

Carbon dioxide is a colorless gas, heavier than the air (sp. gr. 1.529), hence may be collected by downward displacement. Under 50 atmospheres pressure it is liquefied at ordinary temperatures (Faraday); at 36 atmospheres pressure and 0° it forms a white snow, which melts at − 78°. When the liquid is vaporized by diminishing the pressure, this snow is readily produced. The temperature of the snow is −60°. The solid is a poor conductor of heat and vaporizes slowly. When it is evaporated in a vacuum, a temperature of −100° is attained. The liquid is colorless, with specific gravity of 0.91; specific gravity of the solid, 0.83. At the temperature of fusion of the solid the tension equals 3.5 atmospheres; the liquid has that tension at that temperature. If the pressure is less than 3.5 atmospheres, no liquid is formed; the solid vaporizes. Many other solids behave in this way. Ice melts at 0°; its tension is 4.6 mm. If the external pressure is lower, *i.e.*, in vacuo, ice does not melt to water, but vaporizes at once.

It is neither combustible nor a supporter of combustion. It extinguishes ordinary flames. Upon this property depends its use in fire extinguishers, as in hand grenades. Some very powerful combustions, however, can continue in it. Burning magnesium decomposes it: —

$$2\ Mg + CO_2 \overset{\longrightarrow}{\relbar\relbar} 2\ MgO + C.$$

Although a very stable compound, it can be decomposed by an electric spark, and it dissociates partially into CO and O at +1300°. Glowing carbon reduces it to carbon monoxide: —

$$C + CO_2 \leftrightarrows 2\,CO.$$

It is soluble in water, volume for volume. The water solution, "carbonic acid," is weakly acid, reddening blue litmus paper. All natural waters contain more or less CO_2. The amount of CO_2 absorbed by water varies with the temperature and the pressure, as gases are condensed in proportion to the pressure (Law of Henry and Dalton). One volume of water dissolves 2 volumes of CO_2 at 2 atmospheres pressure, 3 at 3, and so forth. When this extra pressure is removed, the liquid *effervesces* through the escape of the excess of CO_2. Upon this depends its use in effervescent drinks.

Carbon dioxide is not an active poison. Animals become asphyxiated in an atmosphere of it on account of the lack of oxygen.

Carbon monoxide, CO, m. wt. 28. When in the combustion of coal the temperature reaches + 700° or higher, or the CO_2 produced at the lower temperatures comes into contact with more carbon, carbon monoxide is produced: —

$$2\,C + O_2 \rightarrow 2\,CO, \text{ and } CO_2 + C \rightleftarrows 2\,CO.$$

Glowing coals at a moderate temperature burn without flame, but from + 1000° upward there is flame. The lambent blue flame observed over a hot anthracite coal fire is the carbon monoxide burning back to the dioxide: —

$$2\,CO + O_2 \rightleftarrows 2\,CO_2.$$

On account of the non-luminous flame produced by its burning, carbon monoxide was mistaken for hydrogen for a long time.

It may be prepared by the method cited above, or by the decomposition of certain compounds. For instance, formic acid has the formula H_2CO_2. If we treat it with a substance which will abstract water, we obtain the monoxide: —

$$H_2CO_2 \rightarrow H_2O + \uparrow CO.$$

It is prepared commercially, and used extensively, by passing steam over hot carbon (coke), "water gas" being produced: —

$$C + H_2O \rightarrow H_2 + CO.$$

Carbon monoxide is a colorless, tasteless, almost odorless gas. It has a specific gravity of 0.967 (1 l. weighs 1.25 g.). It is condensed to a liquid, b.-p. − 190°. It is only slightly soluble in water, 1 : 30, and forms no acid with it, but is dissolved in a solution of cuprous chloride (Cu_2Cl_2), forming a crystalline compound, which is decomposed on heating, with the liberation of the gas. It burns with a beautiful blue flame to carbon dioxide. It will remove oxygen from some metallic oxides when heated with them:

$$CuO + CO \rightarrow Cu + \uparrow CO_2;$$
$$Fe_2O_3 + 3\,CO \rightarrow Fe_2 + \uparrow 3\,CO_2.$$

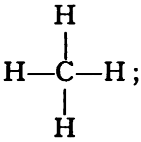
These reactions are utilized technically. It also reduces the salts of some metals, like gold and palladium, precipitating the free metal. Under the influence of gentle heat (+ 50°) it combines with certain metals, especially nickel, to form a gaseous compound, nickel carbonyl [$Ni\,(CO)_4$], which on elevation of temperature (+ 250°), decomposes with the separation of the nickel and re-formation of the gas. The metal may thus be picked up in one place, transferred as a gas, heated and deposited in another, and the transporting agent (CO) cooled and used over again (Process of Mond for the extraction of nickel).

Carbon monoxide is a direct and cumulative poison. The normal function of the hemoglobin of the blood is to form a compound with oxygen, oxy-hemoglobin. The last mentioned, in arterial blood, acts as a carrier of oxygen to the capillaries. Carbon monoxide combines with hemoglobin to produce a more stable compound, carboxy-hemoglobin, which gives the blood a bright red color, to be sure, but prevents the fulfillment of its function. When about one third of the hemoglobin has entered into combination with carbon monoxide, death results. The presence of 0.05 per cent of carbon monoxide in air that is breathed constantly is dangerous. Carbon monoxide readily passes through red-hot iron. Red-hot stoves or ovens, especially when the draught is closed and the ventilation poor, are often the causes of slight poisoning by carbon monoxide, as is evidenced by the dullness and headaches experienced by occupants of rooms where such conditions obtain. Carbon monoxide is produced in tobacco smoke and exhibits its toxic action after excessive smoking.

By a complicated method a lower oxide, carbon suboxide, C_3O_2, may be obtained as a liquid at $+ 7^\circ$ (Diels). It has a very penetrating odor and is solely of scientific interest.

By a brief recapitulation of the hydrogen and oxygen compounds of some of the elements we have considered, most interesting relationships are observed. A molecule of hydrogen consists of two atoms. We may, for convenient illustration, write it, H—H. A molecule of hydrogen chloride is apparently the same, with 1 H substituted by 1 Cl; H—Cl. In CH_4 we may substitute one or all four hydrogen atoms by chlorine, hence 1 H and 1 Cl appear to be equivalent; that is, we may substitute atom for atom. A molecule of water, H_2O, may be written H—O—H. Later we shall learn of Cl_2O, which may be written Cl—O—Cl. Apparently 1 O requires 2 H or 2 Cl as its equivalent for substitution. We have learned of the compounds HCl, H_2O, H_3N, and H_4C. And as 1 O is equivalent to 2 H, we should be able to replace 2 H by 1 O; for example, in H_3N, HON (which is known) and in H_4C, H_2OC (which we shall learn about) and O_2C (or CO_2), which we have studied. This property of an element to substitute another, atom for atom, or a multiple, is known as *valence*. Hydrogen is the unit. When an atom of any element combines with one atom of hydrogen, or its equivalent, it is said to be univalent. If two atoms of hydrogen, or its equivalent, are necessary, as for oxygen, bivalent; if three, as nitrogen, trivalent; if four, as carbon, quadrivalent; and so forth.

This property of the elements is not inherent, but dependent upon a number of conditions, and variable. For example, we have considered two oxides of carbon, CO_2 and CO. The valence of the oxygen or carbon must vary. If we write the compounds graphically, that becomes more apparent:



$$H-\overset{\displaystyle H}{\underset{\displaystyle H}{\overset{|}{\underset{|}{C}}}}-H;\quad H-O-H;\quad O=C=O;\quad C=O.$$

The lines mean nothing more than a graphic illustration of the direction of the attractive force which holds the atoms together in the molecules. We know little of the actual structure of the molecule. When the element exhibits its highest valence (CO_2), we say it is *saturated;* when not (CO), *unsaturated.* The suboxide of carbon is easily explained in terms of valence in this manner; $O=C=C=C=O$, in which the carbon is consistently quadrivalent and the oxygen bivalent.

As many of the elements form compounds with hydrogen, whose univalence, as far as we are aware, is constant, and nearly all of the elements form compounds with oxygen, about the bivalence of which there is only slight suspicion, we may classify the elements according to this property.

EXERCISES

1. How much carbon dioxide may be obtained from 22 g. calcium carbonate?

2. Suppose two volumes of carbon monoxide were burned with oxygen, how many volumes of the latter would be necessary, and how many volumes of carbon dioxide would be produced?

3. Why is it that liquefied carbon dioxide forms the solid as soon as it is exposed to atmospheric pressure?

4. Explain the effervescence of carbonated waters.

5. Illustrate what is meant by valence.

CHAPTER XVI

THE PERIODIC LAW

HYDROGEN was arbitrarily selected for beginning our study of the chemical elements. In continuing it certain resemblances were observed among the members of two separate groups, namely, the halogens and alkali metals. In looking for an orderly and systematic arrangement of facts, we classify on the basis of resemblance. Classification is most helpful as a guide in investigation, as relations are suggested among the facts observed and indications appear whereby new facts of more or less value may be secured. The immediate object of this chapter is to lay out a plan of the relationships of the elements, the pursuit of which will facilitate their further consideration.

There have been presented so far four characteristic properties of all the elements. We shall therefore use them as bases for classification.

1. *Chemical Affinity, or Quality of Combining Power.* This is a primitive, permanent, constant force depending wholly upon the nature of the unchanged atom, and is characteristic of all atoms known, except the "noble gases," which appear to be devoid of it. These elements may, therefore, be set aside as one family. All evidences of chemical affinity among the other elements are accompanied by other forms of energy, hence we have no way of measuring affinity. If we had means for measuring chemical affinity, as we may measure an electric current or heat, a permanent classification on this basis would be possible. We can roughly classify atoms by this property,

however, as they vary widely in their chemical character; for example, the halogens combine vigorously with hydrogen and only by indirect means with oxygen; the alkali metals act in the reverse way. Nitrogen combines with both, but not readily or directly with ease.

2. *Valence, or Quantity of Combining Power*, as we have learned, means the ability of an atom to hold a certain number of other atoms in union, forming a compound. This bears no definite relation to the combining power, that is, whether strong or weak. Valence is not an inherent property of any one atom, but, in part, it is dependent upon the influence the atoms have upon each other in compounds, and is variable. Nitrogen in ammonia is trivalent (NH_3). Ammonia combines directly with hydrogen chloride (HCl) to produce ammonium chloride (NH_4Cl), in which compound the nitrogen is quinquivalent. Phosphorus forms two compounds with chlorine and two with oxygen: PCl_3 and PCl_5, P_2O_3 and P_2O_5. The atoms may be classified, in a measure, according to the valence, but the classification is not based upon a fixed property.

3. *Electro-chemical Character.* We have seen that some binary compounds may be decomposed by an electric current, one constituent going to the positive and one to the negative pole (H_2O, HCl, $NaCl$). Hence, we have electro-negative and electro-positive atoms. At one time the elements were divided into two great classes, the *metals* (electro-positive) and *non-metals* (electro-negative). In fact, this rough subdivision serves a good purpose even to-day. The non-metallic group includes boron, carbon, silicon, nitrogen, phosphorus, arsenic, oxygen, sulphur, selenium, tellurium, and the halogens. Some of them combined with hydrogen (HCl, HBr, H_2S), some combined with hydroxyl [$B(OH)_3$, $ClOH$], and the oxides of some combined with

water (H_2O, $SO_3 = H_2SO_4$), produce acids. The oxides of the metals combined with water give hydroxides or bases [$NaOH$, $Ca(OH)_2$, $Fe(OH)_3$].

The difference in the intensity of the electro-chemical character of different elements is often very pronounced; as, for example, the alkali metals and the halogens are diametrically opposed to each other. Chlorine and iodine are both electro-negative, but the former replaces the latter in binary compounds, hence appears to be more strongly electro-negative. Sodium and silver are electro-positive, but the former is more so. In other words, there are different degrees of electro-positive and electro-negative properties. Furthermore, when hydrogen and arsenic combine (AsH_3), arsenic is negative, but when arsenic combines with oxygen (As_2O_3), arsenic is positive. Therefore, the electro-chemical character of an element is not absolute but relative. There is no unit of measure or standard known by which the electro-chemical property can be accurately determined.

4. *Classification by Atomic Weights.* The atomic weight is a constant value determinable in terms of a standard, hence is fixed and, being capable of exact measurement, may be used in the classification of the elements. Any acceptable method of classification must, however, provide for the other three bases referred to. In 1863 Newlands arranged some of the elements in the order of the increase of the atomic weights, in this manner:—

1	2	3	4	5	6	7
Li, 7	Be, 9	B, 11	C, 12	N, 14	O, 16	F, 19
8	9	10	11	12	13	14
Na, 23	Mg, 24	Al, 27	Si, 28	P, 31	S, 32	Cl, 35.5
15	16					
K, 39	Ca, 40, and so forth.					

All except half fractions in the values are eliminated for convenience. Hydrogen is omitted. It was observed that the eighth and fifteenth elements exhibited properties similar to the first; the ninth and sixteenth similar to the second, and so forth. Newlands presented such a fantastic picture of the "law of octaves" in nature that his suggestion failed to receive serious consideration.

In 1869, Mendelejeff, and the year following Lothar Meyer, independently, propounded the *Periodic Law*, which is based apparently upon the fact that *all the properties of the elements are periodic functions of their atomic weights.** We may secure a clearer understanding of this, if the elements are tabulated in a modified form (p. 108), but a thorough comprehension must await a further study of the elements. This much we may note, however, the alkali metals appear in one column, so do the halogens. They stand at the extreme ends of the table, which may serve to show their marked difference in electrochemical properties. The heavy zigzag line in the upper right-hand corner also serves to mark off the so-called nonmetals. Furthermore, it will be noted that two elements are marked with an asterisk (*), namely yttrium and indium. The places occupied by these two elements were blank when Mendelejeff made his table. The elements were known, but they were regarded as bivalent, with an equivalence of 29^+ and 38^+ respectively, or atomic weights of 58^+ and 76^+. As there were no places in the table for elements with such values, Mendelejeff said that the values were wrong. Investigation subsequently showed he was right and that they are trivalent, hence the

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* A complete history of the inception and formulation of this important generalization is had in "The History of the Periodic Law," Venable, Chemical Publishing Co.

A MENDELEJEFF TABLE — MODIFIED

Li 7											Be 9	B 11	C 12	N 14	O 16	F 19
Na 23											Mg 24.3	Al 27	Si 28.3	P 31	S 32	Cl 35.5
K 39	Ca 40	** Sc 44	Ti 48	V 51	Cr 52	Mn 55	Fe 56	Co 59	Ni 58.7	Cu 63.6	Zn 65.4	** Ga 70	** Ge 72.5	As 75	Se 79.2	Br 80
Rb 85.5	Sr 87.6	* Yt 89	Zr 90.6	Cb 93.5	Mo 96		Ru 101.7	Rh 103	Pd 106.7	Ag 108	Cd 112.4	* In 115	Sn 119	Sb 120	Te 127.5	I 126.9
Cs 133	Ba 137.4	La 139	Ce 140													
				Ta 181	W 184		Os 191	Ir 193	Pt 195	Au 197	Hg 200	Tl 204	Pb 207	Bi 208		
	Ra 226.4		Th 232.4		U 238.5											

accepted atomic weights became three times the equivalence, or 89 and 115, respectively.

Again the places marked with the double asterisk (**) were blank. Considering the positions among the known elements occupied by these "blanks," Mendelejeff predicted not only their discovery, but foretold their properties with surprising accuracy.

According to the statement of the law, if we know the atomic weight, we should be able to place the element in the ascending scale, and its properties should accord with its location. It happens, however, that the facts as they have been observed are not always in accord with this statement. Cobalt has a larger atomic weight than nickel, and tellurium has a greater value than iodine, yet they are placed ahead of those elements in the table. This was done on account of the known physical and chemical properties of these elements, which indicated their family relationship. In a way, therefore, they must be regarded as exceptions to the law, for the time being at least, although so far no satisfactory mathematical relationship among the figures representing the atomic weights has been secured.

We are now ready to look at the most modern table, which will be followed, in a measure, from now on (p. 110).

In this compact table several important points are to be noted. First, the valence in terms of hydrogen increases (as indicated) from Group I to Group IV, and then decreases to Group VII. The valence in terms of oxygen increases consistently through Group VIII. The last group (VIII) contains those elements with atomic weights close together, and which resemble each other physically and chemically to a marked degree. Second, as the "noble gases" show no valence, they are placed in a separate Group O. Third,

THE PERIODIC ARRANGEMENT OF THE ELEMENTS, ACCORDING TO MENDELEJEFF*

On the basis of O=16

Period	*Group O* - -	*Group I* RH R_2O	*Group II* RH_2 $RO(R_2O_2)$	*Group III* RH_3 R_2O_3	*Group IV* RH_4 $RO_2(R_2O_4)$	*Group V* RH_3 R_2O_5	*Group VI* RH_2 $RO_3(R_2O_6)$	*Group VII* RH R_2O_7	*Group VIII* $RO_4(R_2O_8)$
1		H=1.008							
2	He=4	Li=7	Be=9.1	B=11	C=12	N=14.01	O=16	F=19	
3	Ne=20	Na=23	Mg=24.3	Al=27 1	Si=28 4	P=31	S=32.06	Cl=35 46	
4	A=39 9	K=39.1	Ca=40 1	Sc=44.1	Ti=48.1	V=51.2	Cr=52 1	Mn=54.9	Fe=55.85, Co=58.97, Ni=58.7
5		Cu=63.6	Zn=65.4	Ga=70	Ge=72 5	As=75	Se=79.2	Br=79.92	
6	Kr=81.8	Rb=85.5	Sr=87.6	Yt=89	Zr=90.6	Cb=93.5	Mo=96	– =100	Ru=101.7, Rh=102.9, Pd=106.5
7		Ag=107.88	Cd=112.4	In=114.8	Sn=119	Sb=120.2	Te=127 5	I=126.92	
8	Xe=128	Cs=132.81	Ba=137.4	La=139	Ce=140 25	(Pr=140 6)	(Nd=144)	– =149	Sm=150.4, Eu=152, Gd=157 3
9		-	-	Er=167.4	-	Yb=172	-	-	
10		-	-	-	-	Ta=181	W=184.0	-	Os=190.9, Ir=193.1 Pt=195
11		Au=197.2	Hg=200	Tl=204	Pb=207.1	Bi=208	-	-	
12		-	Ra=226 4	-	Th=232.4	-	U=238.5	-	

Some of the rare-earth metals (Vc=117, Tb=159.2, Dy=162.5, Ho=165, Tm=171, Lu=174, etc.) not placed.

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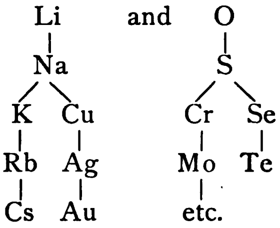
* Revised by the author.

certain of the rare elements, the compounds of which are fairly well known, are placed in the table where the atomic weights call for them. Yet some of these elements are not placed at all. Fourth, hydrogen is placed in a horizontal period (Group I, Period I) alone, as there is no other place for it, and it fits the position. Fifth, the table satisfies the demands of classification by chemical affinity, valence, and electro-chemical properties, which facts will become apparent in due time.

The first period of seven (horizontal line 2) contains the group elements, or *bridge-elements*, since they show many close analogies to the elements in the immediate neighboring groups, while the second period (line 3) gives us the *type-element* of the group. The properties of the other members may usually be defined by their differences from the type. The vertical group then branches into two series, a positive (left) and negative (right). For example,



On the positive side, the members of the positive series show a close relationship to the type-element, while in the negative groups those in the negative series are more like the type. As we pass down the electro-positive series, that property becomes more pronounced. Cæsium is the most positive of the alkali metals. As we pass down the electro-negative series, that property becomes less pronounced. Bromine, while electro-negative, is less so than chlorine.

Iodine is even less so; in fact from its physical properties it appears metallic.

No human document is perfect; this is, however, the best classification of the elements we have at present. Certainly the reader will find it most useful, as he gradually becomes familiar with it and observes not only the kinship of the elements, but the attractive fields awaiting further investigation. The periodic law is one of the most important of the recent generalizations, and has been of the greatest service in the study of the chemical elements and their compounds.

EXERCISE

Refer to the chapters on the halogens and alkali metals, trace their resemblances, and note the gradation of properties.

CHAPTER XVII

GROUP VI.—NEGATIVE SERIES: OXYGEN, SULPHUR, SELENIUM, TELLURIUM

THESE elements are bivalent toward hydrogen, giving the compounds H_2O, H_2S, H_2Se, and H_2Te; and quadrivalent or sexivalent toward oxygen, OO_2, SO_2, SO_3, SeO_2, TeO_2, TeO_3. Oxygen having been discussed, we may consider sulphur.

Sulphur, S, at. wt. 32.06, has been known since ancient times. Sulphur (brimstone) occurs free near volcanoes, especially near Mt. Etna, mixed with gypsum and other minerals, and in the pores of pumice stone. Large deposits have also been found in Louisiana. It occurs combined as sulphides, as iron sulphide (pyrite, FeS_2), galena (PbS), zinc blende (ZnS), or with oxygen and a positive element in the form of sulphates, as gypsum ($CaSO_4$) and barite ($BaSO_4$). It is present in all albuminoid substances of animal and vegetable matter. Some bacteria and algæ contain as much as one fourth by weight of sulphur. Sulphur occurs in abundance and is widely distributed, but is present in very much less amount than oxygen.

It is prepared by three methods:—

1. From the native sulphur by melting in kilns, repurifying by distilling and casting in wooden molds (rolled sulphur or brimstone), or by conversion into a vapor and chilling in large brick chambers to a fine yellow powder (*flores sulphuris*), flowers of sulphur. There are different methods for melting the sulphur out of the crude ore, an

important one depending upon immersion of the ore in a liquid (a water solution of calcium chloride) which boils at a higher temperature than the melting point of sulphur. The method which made the Louisiana deposits available depends upon heating the rock deep down by means of superheated or high-pressure steam. The sulphur is melted and then forced to the surface mingled with hot water. It is sometimes dissolved in a suitable solvent, which is evaporated and used again.

2. Sulphur is also obtained, in small quantities, by heating certain of the natural metallic sulphides without the presence of air, as pyrites: —

$$FeS_2 = FeS + S.$$

3. Sulphur is recovered from certain waste sulphides in manufacturing processes by converting the solid into H_2S and decomposing that, with oxygen and heat, by means of a catalytic agent, into H_2O and S.

Properties. At ordinary temperatures it is usually a yellow, almost odorless, brittle solid. It melts at + 115° to a thin, amber liquid ($S\lambda$), becoming dark brown and viscid at + 250° ($S\mu$) and again a fluid at + 300°, boiling at + 445°. At + 500° it appears to have eight atoms in the molecule, while at + 1000° two atoms.

It is insoluble in water, but readily soluble in carbon disulphide and sulphur chloride. It is a strongly electronegative element, combining with positive elements to form sulphides, as PbS, ZnS, FeS, and so forth. Finely divided metals, except some of the "noble" ones, when rubbed with sulphur, give sulphides, as HgS. In these compounds with metals S is bivalent. It burns with a blue flame in oxygen, forming SO_2; when oxidized in the presence of water, sulphuric acid, a derivative of SO_3, is formed. Sulphur combines with chlorine directly. In combining with non-metals, like oxygen, it shows variable valence, the maximum being sexivalent.

Four allotropic forms of sulphur are known: —

1. *Octahedral, or Rhombic, Sulphur.* This is the ordinary, native, and stable form; sp. gr. 2.07; soluble with difficulty in alcohol and ether; more soluble in ethereal oils and the hydrocarbons; and very soluble in S_2Cl_2 and CS_2. One hundred parts of the latter will dissolve 46 of sulphur at + 22°. It fuses at + 114.5°. It becomes charged negatively when rubbed with wool.

2. *Prismatic, or Monoclinic, Sulphur.* When sulphur is melted and allowed to cool slowly, long, transparent, needle-like crystals are produced, having the sp. gr. 1.96 and m.-p. + 120°. This changes to the first variety on standing. A substance which under proper conditions exhibits two states of aggregation, crystalline forms, is *dimorphous.*

3. *Plastic, or Insoluble, Sulphur.* When sulphur is boiled and suddenly cooled by pouring into water, it becomes plastic, elastic, and without crystalline form, with sp. gr. 1.92. Only a part of the mass is soluble in CS_2. That which is insoluble is the viscous $S\mu$ in a supercooled state (Alex. Smith). On standing, the rubber-like form becomes brittle and returns to the stable form.

4. *Milk of Sulphur (lac sulphuris).* When a strong acid is added to potassium polysulphide, this reaction takes place: —

$$K_2S_5 + 2\,HCl \rightarrow 2\,KCl + \uparrow H_2S + \downarrow 4\,S.$$

This precipitated form of sulphur is white and finely divided, and is sometimes used in medicine.

Sulphur is used in the manufacture of sulphur dioxide and sulphuric acid, gunpowder, matches, in vulcanizing rubber; in medicine as a parasiticide and gentle laxative; also in various compounds.

Selenium (σελήνη — the moon), Se, at. wt. 79.2, was discovered by Berzelius in 1817. It occurs in much smaller quantities with sulphur in certain pyrites (in dust flues of pyrites burners connected with sulphuric acid works), and also free. It has been found in many places, but is not very abundant.

Selenium has also been had in several modifications. When obtained by treatment of a compound with sulphur dioxide, it is a red, brownish powder, soluble in CS_2. It crystallizes from CS_2, giving red crystals of sp. gr. 4.5. It melts at + 217°, boils at + 660°, giving a yellow vapor. When the fused mass is suddenly cooled, a portion separates as a black substance. When the amorphous variety is heated to about + 100°, its temperature suddenly rises to about + 200°, and it changes to a dark, clear crystalline substance, with sp. gr. 4.8. It has a metallic luster, is insoluble in CS_2, and is a conductor of electricity, which conductivity is increased on exposure to light (Ruhmer lamp). At + 1400° it has two atoms in the molecule. It resembles sulphur very closely, burning with a blue flame, the fumes having the odor of decaying horse-radish. It is less powerfully electro-negative than sulphur.

Tellurium (*tellus* — the earth), Te, at. wt. 127.5, was discovered by Muller von Reichenstein in 1782. It is found native and in certain gold ores and as sylvanite. It is precipitated by SO_2 as a black powder, with sp. gr. 5.9. When fused, it forms a silvery white solid with a metallic luster; sp. gr. 6.4; m.-p. + 454°; b.-p. + 1390°. It conducts electricity and burns with a blue flame. At + 1700° its vapor has two atoms in the molecule.

According to the periodic law, tellurium should have an atomic weight of approximately 125, or iodine should show a value above that of tellurium. Numerous efforts to show that tellurium is complex, that it contains another element, heavier (at. wt. 214), which would bring tellurium to a lower figure, have been made in vain (Brauner, Norris, Lenher). The same has been true of all efforts to find a lighter element in iodine, which would make the value of real iodine sufficiently high to be above that of tellurium (T. W. Richards). At present we simply acknowledge a defect in the *law.*

EXERCISES

1. What is the molecular weight of rhombic sulphur at ordinary temperatures?

2. What is the molecular weight of sulphur, selenium, and tellurium above + 1700°?

3. Tabulate the physical properties of the four elements considered in this chapter, and state any general principles that may be drawn from the facts so collated.

CHAPTER XVIII

GROUP V.—NEGATIVE SERIES: NITROGEN, PHOSPHORUS, ARSENIC, ANTIMONY, BISMUTH

THESE elements show little physical resemblance, but have much in the way of chemical properties in common. This we shall observe especially when we study their compounds with hydrogen, the halogens, and oxygen.

Nitrogen has been considered.

Phosphorus was discovered in 1669 by the merchant-alchemist Brand, who distilled the residue from evaporated urine. Gahn found calcium phosphate [$Ca_3(PO_4)_2$] in bones, and Scheele separated the phosphorus from it.

On account of its strong affinity for oxygen, phosphorus always occurs combined with it in phosphates, as apatite, $Ca_5(PO_4)_3F$. It occurs widespread in small amounts in rocks and soils, from which it is taken up directly by plants and indirectly by animals. It is found in the ashes of cereals. Large phosphate deposits are found in South Carolina, Florida, Canada, Algiers, Spain, and Japan. Calcium phosphate constitutes more than three fourths of the mineral matter of bones.

It is prepared by mixing the ground phosphate with carbon and sand and heating:—

$$Ca_3(PO_4)_2 + 3\,SiO_2 + 5\,C \underline{\rightarrow} 3\,CaSiO_3 + \uparrow 5\,CO + \uparrow 2\,P.$$

This is best accomplished by feeding the mixture continuously into a retort near the bottom of which are the terminals of a powerful alternating current, which is thermal in its action. The calcium metasilicate ($CaSiO_3$) fuses and runs to the bottom, from which it is drawn off from time to time. The CO and vapors of P pass out through pipes near the top and are bubbled through water. The P is liquefied, settling in the water, and the escaping CO is burned. The phosphorus is melted in warm water, strained through chamois, and cast in glass or tin molds. It is absolutely necessary to avoid the mixing of any air or oxygen with the vapor of phosphorus.

Three allotropic forms of phosphorus are known; the properties are conveniently compared in tabular form: —

Yellow	Red	Metallic
[Brand (1669)]	[Schrötter (1845)]	[Hittorf]
Pale yellow	Chocolate red	Lustrous
Strong odor	Odorless	Odorless
Sp. gr. 1.83	2.20	2.34
Phosphorescent	Not	
Translucent	Opaque	
Soluble in CS_2	Insoluble	
Subject to slow combustion	Not	
Melts at +44° C.	About +255° C.	
Changes to red +300° C.	Changes to yellow +260° C.	
Soft	Hard	
Flexible (ord. temp.)	Brittle	
Poisonous	Harmless.	
Rhombic crystals	Hexagonal	Needles
Takes fire +40° C. or with friction	Stable form	
Boils +287° C.		

The phosphorus molecule, which is dissociated above + 1040°, has four atoms in it. The yellow variety is insoluble in water, but soluble in oil of turpentine and carbon disulphide. It is very poisonous in the finely divided form or as a vapor. In chronic poisoning by phosphorus the teeth are affected and necrosis of the jaw-bone is produced. It combines readily with oxygen to form P_2O_3 or P_2O_5, burning with a green flame. It combines vigorously with the halogens; causes precipitation of metals in copper sulphate and silver nitrate solutions. At ordinary temperatures it oxidizes slowly with luminosity in the dark, hence its name. Its phosphorescence is not observed when it is under great pressure or in pure oxygen, unless the pressure is reduced to about 150 mm. As it is so readily oxidized, it must be kept under water. Great care must be taken in handling yellow phosphorus, as serious burns may result. It takes fire spontaneously when left exposed to the air. It should not be rubbed in drying it, but gently pressed with blotting paper. The yellow form on exposure to light becomes covered with a coating of the red form. This is an exothermic change (+19.2 cal.).

The yellow variety was at one time used in making matches, but its use for such purposes is now much restricted by law. It is used in making organic compounds and vermin paste. The red form is used extensively in making matches, the heads of which are frequently composed of red phosphorus and potassium chlorate bound together with glue. "Safety" matches often have the heads made of antimony sulphide (Sb_2S_3), potassium chlorate, and glue. The surface upon which they are rubbed to ignite them is composed of sand (or emery), manganese dioxide (MnO_2), and red phosphorus.

Arsenic occurs free in nature, its metal-like properties having been observed by the alchemists. It is found more abundantly with sulphur and combined with metals, as realgar (AsS), orpiment (As_2S_3), arsenopyrite (FeAsS), löllingite ($FeAs_2$). Lately it has been reported as a constituent, in very minute amounts, of the animal body (Gautier).

When we heat a binary compound of sulphur or arsenic in the air, the sulphur is burned to a gas, sulphur dioxide (SO_2), and arsenic to a white solid, arsenic trioxide (As_2O_3), which sublimes at the temperature it is formed. By cooling the gases evolved the arsenic trioxide condenses as a white flour. This process of oxidation to remove volatile constituents is technically known as *roasting*. In the case of arsenical pyrites the reaction takes place as follows: —

$$2\ FeAsS + 5\ O_2 \rightleftarrows Fe_2O_3 + As_2O_3 + \uparrow 2\ SO_2.$$

The iron oxide remains in the roasting furnace, the sulphur dioxide is sent into the air or saved by methods referred to later, and the arsenic trioxide is collected by cooling. The escaping gases are passed through thin-walled chambers, usually wooden houses built with the weather boarding inside the rafters and studs. The "arsenic flour" is mixed with carbon and placed in iron kettles, built up of sections and provided with long thin-walled exit tubes to insure thorough cooling of the gases given off.

$$As_2O_3 + 3\ C \rightleftarrows 2\ As + \uparrow 3\ CO.$$

Many thousand tons of iron pyrites are annually roasted in the manufacture of sulphuric acid. Arsenical pyrites is a constant and usually small impurity of the iron pyrites. Most of the arsenic trioxide collects as dust in the flues, but some of it is swept on, and constitutes an impurity in the acid and in many products subsequently obtained by the use of the acid.

Arsenic is known in three modifications. One is an amorphous, black, brittle solid; sp. gr. 4.71. When heated to + 360°, it changes into the second form, which is steel-gray, with metallic luster; sp. gr. 5.73. There is also a yellow variety soluble in carbon disulphide. At + 450° it sublimes with a yellow vapor. At + 1700° it has two, while at + 700° it has four, atoms in the molecule. It is not changed in dry air, but takes fire at + 180°, burning with a blue flame, forming As_2O_3, which as a vapor has a garlic-like odor. It is insoluble in water and the ordinary solvents. It is a weakly negative element, combining with positive elements to form arsenides; also with more negative elements like chlorine, sulphur, and oxygen.

Arsenic is used in making its compounds and in certain alloys; 1 : 1000 of lead makes it hard. "Chilled" shot is made from this alloy.

Antimony. Basil Valentine, about the end of the fifteenth century, first described the preparation of the metal. This was not a new discovery, however, as some of its compounds have been known from the earliest times, and used as pigments. Pliny refers to stibnite as *stibium*. The native sulphide, or stibnite, was called "kohl" in Arabic, which was gradually changed to "alkol" and later to "alkohol." In the Middle Ages the term was applied to almost any fine powder, and later spirits of wine.

The occurrence of antimony is similar to arsenic. They often occur together. It is found free and as stibnite, Sb_2S_3. It is not very widely distributed and is not so abundant as arsenic.

It is prepared in the same way that arsenic is and also by heating the sulphide with iron: —

$$Sb_2S_3 + 3\ Fe = 3\ FeS + 2\ Sb.$$

The iron sulphide and antimony melt and form two layers, the antimony sinking to the bottom of the furnace, from which it is tapped from time to time.

Antimony is a hard, brittle, steel-gray, brilliant, metallic, lustrous, leafy, crystalline solid, with sp. gr. 6.7, m.-p. + 432°. When heated from + 1500° to + 1700°, it has two atoms in the molecule, while below that it is Sb_4. It burns readily in the air, with a blue flame. With the positive elements it forms alloys, especially type-, stereotype-, and britannia metals. Antimony alloys expand on solidifying, hence give very sharp castings. It combines readily with negative elements and forms a compound with hydrogen.

Bismuth was first described by Basil Valentine, but was probably known earlier.

Bismuth occurs free, but not widely distributed, and not abundantly; and combined as oxide (Bi_2O_3), sulphide (Bi_2S_3), and in small amounts in many nickel and silver ores.

It is prepared by melting away from the veinstone with which it is found.

It is a reddish-white lustrous metal; crystalline and brittle, although slightly workable. It does not burn easily, but heated to kindling temperature in the air, forms Bi_2O_3. It combines chiefly with the negative elements. It forms alloys with low melting points. These alloys are used for safety plugs in steam boilers and sprinklers.

EXERCISES

1. What principles are illustrated by the methods given for the extraction of arsenic, antimony, and bismuth from their ores?

2. In what ways do the physical properties of the members of this series change as the atomic weights increase?

3. Why is it so essential to avoid mixing air with phosphorus vapor?

4. What is the principle involved in roasting?

GROUP V — NEGATIVE SERIES

ELEMENT	NITROGEN	PHOSPHORUS	ARSENIC	ANTIMONY	BISMUTH
Derivation of name . .	Nitrum — saltpeter, and γεννάω — to generate	φῶς — light, and φέρω — bear	ἀρσενικόν	Late Latin — antimonium — stibium	Wismut, which is derived from wiesenmatte
Symbol . .	N	P	As	Sb	Bi
Atomic weight	14.01	31.0	75.0	120.2	208
Discoverer .	Rutherford	Brand	. . . . . .	Basil Valentine	Basil Valentine
Date . . .	1772	1669	. . . . . .	End of 15th century	1450
Physical state	Gas	Solid	Solid	Solid	Solid
Appearance .	Colorless	1. Yellow 2. Chocolate red 3. Metallic	1. Amorphous black 2. Metallic 3. Yellow	Metallic, steel-gray	Metallic, reddish white
Specific gravity	0.972	1. 1.83 2. 2.19	1. 4.71 2. 5.73	6.7	9.8
Melting point	− 214°	+ 44°	+ 480° C. (under high pressure)	+ 430°	+ 270°
Boiling point	− 193°	+ 287°	. . . . . .	About + 1300°	Between + 1100° and + 1450°

CHAPTER XIX

GROUP II.—POSITIVE SERIES: ALKALINE EARTH ELEMENTS

We have now studied all of the so-called non-metallic elements, except silicon, which is intermediate. Its consideration may be conveniently postponed a few pages, while we study the metals in logical sequence, taking those with dominating electro-positive properties first. The positive series of Group I (the alkali metals) has received attention. The positive series of Group II contains what are spoken of as *alkaline earth* elements, because they resemble the alkalies, on the one hand, and the earths (Group III), on the other.

This group of elements is of singular interest. First, because we have two names for the first member. Second, because that member is prepared by a type-method, which has been and is still extensively used in the preparation of the rarer metals. Third, because four members (magnesium, calcium, strontium, and barium) occur naturally in similar compounds (carbonates and sulphates), and were known and mistaken for each other for a long time. Their oxides were regarded as elements up to a century ago. They never occur free in nature. Fourth, all of them are constantly bivalent and form binary compounds with electronegative elements, XO, XCl_2, XBr_2, and so forth. And fifth, the heaviest member of the group has been known only a decade and possesses properties (in its compounds — we do not know the free element) which are causing a recasting of many of the fundamental concepts of the science of chemistry.

Beryllium (glucinum) occurs in the mineral beryl [$Be_3Al_2(SiO_3)_6$].

It is prepared by heating the halogen compound with a more strongly electro-positive element: —

$$BeCl_2 + Na_2 \rightleftarrows 2\ NaCl + Be.$$

This method is applicable to at least the first five members of the series.

This rare metal looks like the familiar magnesium. The compact form does not readily oxidize on heating to a high temperature, but when finely divided it burns with great brilliancy. The salts soluble in water have a sweet taste, hence the alternate name. Other metallic salts are also sweet; therefore, if there were no other reason, preference should be given to the more distinctive name.

Magnesium. Black first pointed out the distinction between magnesium and calcium oxides. Its compounds are widely distributed and are more or less abundant, as magnesite ($MgCO_3$), dolomite ($MgCO_3, CaCO_3$), and silicates, as meerschaum, talc, soapstone, olivine, and asbestos. Sulphates and chlorides occur in sea water and in certain salt deposits.

It is a malleable metal, tarnishes in the air slowly at ordinary temperatures; at an elevated temperature it burns with a brilliant, white light, which is rich in so-called chemical or actinic rays. The temperature of burning magnesium is between + 1300° and + 1400°. The intense light comes in large part from the chemical energy involved, for if it were due to incandescence, a temperature of at least + 5000° would be necessary to produce light of that character. Heated magnesium combines directly with nitrogen to form the nitride (Mg_3N_2); therefore, when magnesium is burned in the air, the oxide produced is mixed with nitride.

On account of its strong affinity for oxygen, magnesium is used to reduce some of the oxides of the rare metals. It is readily soluble in acids. Mixed with potassium chlorate, it is used for flash-lights.

Calcium was first isolated by Davy by means of the direct electric current, and all these metals are now so prepared commercially.

It occurs as carbonate (limestone), sulphate (gypsum), fluorspar (CaF_2), and in numerous silicates and phosphates. It is widely distributed and abundant. It is found in plants, and its compounds are constituents of the bones and shells of animals.

It is a little harder than lead, may be cut, rolled, and drawn. It decomposes water at ordinary temperature, evolving hydrogen. When heated to redness in the air, it burns with a brilliant, orange-yellow flame (CaO). Some nitride (Ca_3N_2) is also produced. It combines directly with hydrogen also (CaH_2), to form a compound commercially known as "hydrolyte."

Strontium occurs as carbonate (strontianite) and sulphate (celestite).

Barium also occurs as carbonate (witherite) and sulphate (heavy spar).

Radium occurs in compounds, the exact combination being unknown. It will be considered in a special chapter.

EXERCISES

1. Give the two type-methods for preparing the alkaline earth metals, and the principles upon which they are based.

2. From the table of comparative properties, observe the relationship of the specific gravities and atomic weights

GROUP II. — POSITIVE SERIES — COMPARISON OF PROPERTIES

ELEMENT	BERYLLIUM (Glucinum)	MAGNESIUM	CALCIUM	STRONTIUM	BARIUM	RADIUM
Derivation of name . .	Beryl, chief source (γλυκύς — sweet)	Magnesia — a district in Thessaly	Calx — lime	Strontian, Argyllshire, Scotland	βαρύς — heavy	Radiant matter
Symbol . . .	Be (Gl)	Mg	Ca	Sr	Ba	Ra
Atomic weight	9.1	24.32	40.09	87.6	137.37	226.4
Discoverer . .	Vauquelin	Black	F. Hofmann	Crawford	Scheele	P. and Mme. Curie and Bémont
Date	1797	1754	1722	1790	1774	1898
Element isolated by .	Wöhler	Davy	Davy	Davy	Davy	......
Date	1828	1808	1808	1808	1808	......
Physical state .	Solid	Solid	Solid	Solid	Solid	Element not yet isolated
Appearance .	White metal	White metal	Yellowish white metal	Metallic	Yellow powder	......
Specific gravity	1.93	1.75	1.58	2.54	3.75	......
Melting point .	< 1000°	+ 750°	+ 760°	red heat	850°	......
Boiling point .	.....	About + 1100°	......	......	......	......
Burns with . .	Bright	White	Orange	Crimson	Green	Purplish color
Action on water . . .	None	Decomposes boiling	Decomposition	Decomposition	Decomposition	......

CHAPTER XX

GROUP III. — THE EARTH ELEMENTS — THE RARE-EARTH ELEMENTS

In this group we are introduced to elements which present several interesting features. First, these elements are primarily metallic in character, yet the oxygen compound of boron is acidic. Aluminum oxide acts as an acid oxide with strong bases, and as a basic oxide with strong acids. Second, the bridge-element is had in a form strikingly like the diamond, and the oxide of aluminum in general physical properties is similar to the magnesium oxide. Third, aluminum ranks third in the relative abundance of the elements, and its oxide, especially when combined with the oxide of silicon, gives us what is termed *earth*. Fourth, aluminum is the lightest metallic element of extensive technical use. Fifth, elements are found in this group which confirm the periodic law, yet some are mentioned that cause us to wish for a more perfect expression of the relationship of the members of the family of elements.

The elements of this group all show a valence of three toward oxygen, X_2O_3, and with the halogens, as BF_3, $LaCl_3$, and so forth. None of them occurs free in nature.

Boron occurs always combined with oxygen and hydrogen, as in boracic or boric acid, or its salts, as borax ($Na_2B_4O_7$, $10\,H_2O$), boracite ($2\,Mg_3B_8O_{15}$, $MgCl_2$), and colemanite ($Ca_2B_6O_{11}$, $5\,H_2O$).

It is prepared by reducing the oxide with a metal, as

(1) $B_2O_3 + 6\,Na \rightarrow 3\,Na_2O + 2\,B$, and
(2) $B_2O_3 + 3\,Mg \rightarrow 3\,MgO + 2\,B$.

It ignites at +700°; dissolves in melted aluminum, from which it crystallizes on cooling as dark, brilliant crystals (sp. gr. 2.6) which resemble the diamond in luster and hardness. It burns with even greater difficulty than the diamond.

Boron is one of the few elements that combine directly with nitrogen. Boron nitride (BN) is formed. It combines with positive elements in the electric furnace, giving borides, some of which are of commercial importance. At high temperatures it combines with sulphur and chlorine.

Aluminum exists in abundance in compounds, but the difficulty of separating it prevented its early discovery. Soon after 1800 it was recognized that clay contained a new element. In 1827 Wöhler isolated it.

Aluminum always occurs combined, as with oxygen and silicon in clay; in many minerals, as feldspar and mica; in many forms of its one oxide, Al_2O_3, as corundum or emery. It is the chief constituent of many precious stones, like the ruby and sapphire; and of cryolite ($3\,NaF, AlF_3$) and bauxite ($Al_2O_3, 2\,H_2O$).

The principles involved in the preparation of aluminum present interesting applications of the science of chemistry to industry. It was made for years by the action of metallic sodium upon a double halogen salt: —

$$AlCl_3, NaCl + 3\,Na \rightarrow 4\,NaCl + Al.$$

$AlCl_3$ does not melt, but sublimes, when heated under atmospheric pressure. When mixed with NaCl, it readily melts. The problem of producing cheaper metallic aluminum therefore depended upon cheaper sodium. Castner solved this problem. The price of the metal was reduced, but scarcely was this accomplished before Hall discovered that alumina (Al_2O_3), which is very insoluble, is soluble in a molten double halide, cryolite ($AlF_3, 3\,NaF$), and in that condition could be electrolyzed. Cells with carbon linings acting as cathodes hold the cryolite, which is fused by the passage of a direct current (5 to 6 volts). Aluminum oxide dissolves in the bath. Carbon rods act as anodes and are oxidized by the escaping oxygen, while the freed metal collects as a liquid in the bottom of the cells and is drawn off from time to time.

Aluminum is a white, silvery, lustrous metal. It melts at + 660°, but does not vaporize. It is the lightest metal of structural importance (sp. gr. 2.7). It is fairly tenacious, malleable, and ductile, having about the same softness as silver. It is difficult to turn on the lathe or cut with a file as it adheres to and clogs the tools. It conducts heat and electricity. It does not conduct as well as copper when we compare cross sections, but weight for weight it is a better conductor. It is not sonorous when pure. Usually it is impure, however, and is then sonorous. It does not tarnish readily, not being acted upon by pure oxygen at ordinary temperatures. Under some conditions it tarnishes, but the thin film of oxide formed prevents further oxidation or pitting. It combines with oxygen at high temperatures and thus reduces other substances, liberating free metals. The Goldschmidt alumino-thermic process depends upon this property and is of great practical value. A mixture of aluminum powder and ferric oxide (thermit) is ignited by means of a burning magnesium wire: —

$$Fe_2O_3 + Al_2 \rightarrow Al_2O_3 + 2\,Fe.$$

The temperature attained is about + 3000°. The iron melts, runs to the bottom of the vessel, and is tapped off, and the lighter fused Al_2O_3 forms a protective coating. Very pure metallic preparations are also made from such refractory oxides as those of chromium and manganese. The sulphides are reduced in the same way. The metal is soluble in acids, as vegetable acids, and especially in the presence of salts: —

$$2\,Al + 6\,HCl \rightarrow Al_2Cl_6 + \uparrow 3\,H_2.$$

It is also soluble in certain alkalies: —

$$2\,Al + 6\,KOH \rightarrow 2\,K_3AlO_3 + \uparrow 3\,H_2.$$

Aluminum is used for very many purposes where a light metal is desirable, as, for instance, in scientific instruments, domestic utensils, military accouterments, and air ships; especially is it used for these purposes in the form of alloys, the most important of which are magnalium, an alloy with (6 to 30 per cent) magnesium, aluminum bronze (5 to 12 per cent aluminum), which is easily fusible, of golden luster, with mechanical and chemical resistance superior to ordinary bronze.

The Rare-earth Metals. This group, in both series, as may be seen from the two tables, contains several rare elements. The metals of the *rare-earths* are little known. Many of their compounds exhibit such similarity in chemical conduct that they are difficult of separation. They are found in rare and very complex minerals, especially gadolinite, euxenite, samarskite, monazite, which are found mainly in Sweden, Greenland, United States, and Brazil. Those in this group have so far shown no properties which have caused a commercial demand for them. The high prices quoted in the market for them are largely fictitious values. These elements are interesting because one of them, yttrium, had its atomic weight revised in the working out of the periodic law, two of them, scandium and gallium, were predicted by Mendelejeff in applying the law, and their hidden possibilities await further investigation.

Other of the rare elements are even less known, victorium, thulium, holmium, and so forth, and we do not now know where to place them in the natural system. Either our knowledge of them is too meager, which is very likely, or the periodic law requires further elaboration, which is of equal likelihood. The law has been modified to accommodate the noble gases. Numerous suggestions as to the places for the elements have been put forward, but until we arrive at something fairly definite, it is futile to discuss them in an elementary work.

EXERCISES

1. How much aluminum should we theoretically obtain from an ore containing 90 per cent of bauxite?

2. Assume that "thermit" contains 75 per cent iron oxide; how much of the mixture would be required to produce 6 lb. of metallic iron?

3. Suppose we had a bar of aluminum weighing 1800 g., how many cubic centimeters of water would it displace?

4. How much sodium would be necessary, assuming exact proportions, to produce 3 kg. of aluminum?

GROUP III. — NEGATIVE SERIES

ELEMENT	GALLIUM	INDIUM	ERBIUM	THALLIUM
Derivation of name .	Gallia (Gaul — France)	Indicum—(the spectrum has an indigo blue line)	Ytterby in Sweden	θαλλός — green twig — green line in spectrum
Symbol	Ga	In	Er	Tl
Discoverer	De Boisbaudran	Reich and Richter	Mosander	Crookes and Lamy independently
Date	1875	1863	1843	1861
Atomic weight . .	69.9	114.8	167.4	204
Physical state . . .	Solid	Solid	Element not isolated	Solid
Appearance . . .	Shining, green-blue metal	Platinum-colored metal	. . . . . .	Metal — resembles lead
Specific gravity . .	5.95	7.4	. . . . . .	11.85

GROUP III. — POSITIVE SERIES

ELEMENT	BORON	ALUMINUM	SCANDIUM	YTTRIUM	LANTHANUM
Derivation of name .	Bōraq (Arabic for borax)	Alumen (alum)	Scandia — Scandinavia	Ytterby in Sweden	λανθάνειν (to hide)
Symbol	B	Al	Sc	Yt	La
Discoverer	. . . . . .	Hofmann (Al_2O_3)	Nilson and Cleve independently	Gadolin	Mosander
Date	. . . . . .	1722	1879	1794	1839
Atomic weight . . .	11.0	27.1	44.1	89.0	138.9
Physical state . . .	Solid	Solid	Element not yet isolated	Solid	Solid
Appearance	Brown, amorphous powder and dark crystals	Lustrous, silvery white	. . . . . .	Gray powder	Metallic
Specific gravity . .	2.5	2.7	. . . . . .	. . . . . .	6.15
Melting point . . .	. . . .	657.3°	. . . . . .	. . . . . .	below silver

CHAPTER XXI

GROUP IV.—CARBON-SILICON GROUP

THIS group of elements possesses particular interest because, first, while the bridge-element, carbon, is the backbone of the living world, the type-element, silicon, occupies a similar position for the dead, or mineral world. Second, carbon occurs free, while none of the other elements in this group has ever been found except combined with some other element. Third, while the type oxide is XO_2, the bridge- and type-elements and the negative series also form XO. Fourth, while two members of the negative series (tin and lead) have been known from early times, the third was predicted by Mendelejeff four decades ago and discovered in 1886. Fifth, the group contains thorium, the element with next to the highest atomic weight and one of the parent radio-active substances.

Carbon has been studied.

Silicon (from *silex*— flint), Si, at. wt. 28.4, is never found uncombined, although next to oxygen it is the most abundant element. It is found combined with oxygen, as silica (SiO_2), in the form of quartz, flint, agate, sand, or combined with oxygen and metals, as silicates, like mica, feldspar, and so forth. Its compounds constitute the basis of rocks and of the soil.

It is prepared by the reduction of binary halogen or oxygen compounds by metals. This was the method used by Berzelius in 1810. when he first separated it. It is also prepared by heating the oxide mixed with carbon to very high temperatures in an electric furnace: —

$$SiO_2 + 2\,C \rightleftharpoons Si + \uparrow 2\,CO.$$

Silicon is a dark brown, lustrous powder which does not conduct electricity. It is soluble in molten metals, like zinc, from which it crystallizes as black octahedra and needles; sp. gr. 2.49. It is very hard and fuses only at a white heat, when it may be run into molds. It is not soluble in ordinary single acids, but is in a mixture of hydrofluoric and nitric acids. It combines with the halogens and oxygen and sulphur when heated to from + 400° to + 600°. It combines with positive elements to form silicides, and with carbon to form carborundum, SiC, when subjected to the temperature produced in an electric furnace.

POSITIVE SERIES

Titanium occurs as oxide, rutile, perovskite ($CaTiO_3$), menaccanite ($FeTiO_3$). *Zirconium* is found as zircon ($ZrSiO_4$). *Cerium* occurs as cerite and in monazite. *Thorium* occurs as silicate, thorite, and as phosphate in rare minerals. It is probably complex.

They may be prepared by the method of Berzelius. Recently cerium has been prepared by the Hall process for aluminum (Muthmann).

They are all more or less dark, metallic, lustrous substances which burn in oxygen or air to dioxides. The free metals are not used commercially. The alloys of titanium with iron are useful and the cerium alloy with iron (30 per cent) gives brilliant sparks when filed (devil's touchstone).

COMPARISON OF PROPERTIES OF POSITIVE SERIES

Element	Titanium	Zirconium	Cerium	Thorium
Derivation of name . . .	Titan — a deity	Jargon (Zargūn)	Asteroid Ceres	Scandinavian god of thunder
Symbol . . .	Ti	Zr	Ce	Th
Discoverer . .	Klaproth	Klaproth	Klaproth, and Berzelius and Hisinger, independently	Berzelius
Date	1794	1789	1803	1828
Atomic weight	48.1	90.6	140.2	232.4
Appearance .	Dark gray powder	Glassy crystals	Lustrous malleable metal	Lustrous crystals
Specific gravity	3.54	4.15	7.04	11.00
Melting point .	+ 2500°	+ 1500°	+ 623°	Above + 2500°

NEGATIVE SERIES

Germanium was predicted by Mendelejeff, being called by him eka-silicon, and was discovered by Winkler in 1886 in argyrodite, $3(Ag_2S), GeS_2$.

Tin, probably brought from the British Isles by the Phœnicians, was called *plumbum candidum* according to Pliny, but in the fourth century the word *stannum*, which first meant a mixture of metals, was applied to it. Tin occurs chiefly as the dioxide (SnO_2, cassiterite), and is not widely distributed. It is found mainly in Malacca and Cornwall. The earliest known form of tin was in an alloy with copper, bronze.

It is prepared by roasting to remove sulphur and arsenic combined with the other metals present and then heating the oxide with carbon: —

$$SnO_2 + 2\,C \rightarrow Sn + \uparrow 2\,CO.$$

As the ore usually contains some iron oxide, that and other metals are reduced at the same time and are present as impurities in the metal. They are removed by fusing the impure material at a low temperature, when the liquefied tin runs off and leaves the other metals behind. The process must be repeated several times.

Ordinary tin is a silvery white, lustrous, crystalline, soft, malleable metal. Its crystalline condition is observed in one way by bending a bar of the metal. A cracking sound ("tin cry") is heard as a result of the friction of the crystals. They may also be observed by etching a bar of tin with hydrochloric acid, when remarkable striations appear, or depositing it electrolytically. It becomes brittle when heated to + 200°. It may be rolled into thin sheets (foil).

Under suitable conditions of temperature (+ 20°), white tin changes into a gray powder. Other of its characteristic properties also change; for instance, the specific gravity changes from 7.3 to 5.8. This fact acquires serious importance when it is recognized that this "tin disease" is contagious. Organ pipes made of tin may become utterly useless. The fact has been known since the time of Aristotle. The explanation is very recent. Ice changes definitely and quickly into water at zero. We may cool water below zero, but as soon as we disturb it, ice forms at once. Zero is the transition point of these two physical states. Twenty degrees is the transition point at which ordinary tin takes on its disguise or assumes its unstable allotropic form, for it changes back when the temperature is elevated. The change to gray tin at + 20° requires a long time and is not sudden, like the change of ice to water at 0°, or the change of selenium at + 200°.

It does not tarnish or rust at ordinary temperatures, but burns, when heated in the air, with a brilliant light, forming SnO_2. It combines directly with negative elements and dissolves in hydrochloric and sulphuric acids:

$$Sn + 2\,HCl \overset{\rightarrow}{=} SnCl_2 + \uparrow H_2;$$

and the alkalies:

$$Sn + 2\,KOH + H_2O \overset{\rightarrow}{=} K_2SnO_3 + \uparrow 2\,H_2.$$

It is oxidized by nitric acid and is not dissolved by it. Indirectly SnO may be obtained. When chlorine is passed over the salt produced by the solution of tin in hydrochloric acid, another chloride is formed:

$$SnCl_2 + Cl_2 \overset{\rightarrow}{=} SnCl_4.$$

It will thus be observed that the valence varies. It is bivalent and quadrivalent. When the metals form two classes of compounds with the electro-negative elements, the number of the latter is not only indicated by the Greek numerical prefix, as tin monoxide, dioxide, or tin dichloride, tetrachloride, but also by variations in the ending of the name of the electro-positive element; for example, stann*ous* oxide (SnO), stann*ous* chloride ($SnCl_2$), and stann*ic* oxide (SnO_2), and stann*ic* chloride ($SnCl_4$).

On account of its malleability, ductility, and unalterability on exposure to air, tin is a valuable metal, and is extensively used as block tin and in making tin-plate, which is essentially a thin sheet of iron covered with a film of tin. Tin is a constituent of important alloys, as brass, bronze, solder, bell metal, and so forth.

Lead was one of the earliest known metals. For a long while it was not clearly distinguished from tin. Pliny called it *plumbum nigrum* to distinguish it from *plumbum candidum.* The Romans knew of lead and constructed waterways out of it.

It occurs mainly as the sulphide (PbS, galena), carbonate ($PbCO_3$, cerussite), chromate ($PbCrO_4$, crocoisite), and molybdate ($PbMoO_4$, wulfenite).

The preparation of lead illustrates the application of purely scientific facts to metallurgical economy. When lead sulphide is roasted, the oxide is formed:

$$PbS + 3\,O \rightarrow PbO + \uparrow SO_2.$$

The oxide heated with carbon is reduced to the metal:

$$PbO + C \rightarrow Pb + \uparrow CO.$$

But as sulphur combines with oxygen, as shown in the first equation, the roasting is carried so far that only two thirds of the sulphide have been oxidized; the furnace is then closed to shut out air, and the heat continued at an elevated temperature:

$$PbS + 2\,PbO \rightarrow 3\,Pb + \uparrow SO_2.$$

The cost of the carbon is saved and a part of the ore acts as the reducing agent. Lead is always impure when first prepared, as its ores carry variable amounts of gold and silver. The purification of lead may, therefore, be considered more conveniently later.

Lead is a soft, workable metal, whose surface freshly exposed is bluish white and lustrous. It is not very strong. Its crystalline condition may be shown by etching with nitric acid or separation from its solutions by zinc (lead tree).

While warm it is squeezed by hydraulic pressure into pipes used in plumbing and to cover electric cables. Lead, as usually seen, is dull gray. It readily tarnishes on exposure to the air, but the oxidation is superficial. When placed in pure water containing oxygen, it forms $Pb(OH)_2$, which is soluble. If carbon dioxide is present also, the hydroxide is converted into a carbonate, which does not dissolve easily in the water. Hard waters bring about the formation of a coating of the carbonate and sulphate, which protects the lead from further corrosion. Lead is

COMPARISON OF THE PROPERTIES OF THE NEGATIVE SERIES

Element	Germanium	Tin (Stannum)	Lead (Plumbum)
Derivation of name	Germania	. . . . . .	. . . . . .
Symbol	Ge	Sn	Pb
Discoverer . . .	Winkler	Known in early times	Known in early times
Date	1886	. . . . . .	. . . . . .
Atomic weight . .	72.5	119.0	207.1
Appearance . . .	Lustrous	Lustrous	Soft, lustrous metal
Specific gravity . .	5.47	7.29	11.37
Melting point . .	+ 954°	231.5	322°
Boiling point . .	. . . . . .	> 1600°	> 1600°

insoluble in dilute hydrochloric and sulphuric acids, but is readily soluble in nitric acid. On account of its insolubility, sheet lead is extensively used in chemical works, especially in building sulphuric acid chambers.

Lead in soluble forms is a cumulative poison, producing "lead colic," "wrist drop," and so forth, often observed in house painters. Lead forms the basis of a number of useful alloys, as type-metal, bird shot, solder, and so forth.

EXERCISES

1. If the temperature is regulated, PbS may be roasted in part to $PbSO_4$. Write the reaction showing the separation of lead by heating these two together.

2. Iron when heated has a stronger attraction for sulphur than lead, bismuth, or antimony. Write the reaction by which lead may be separated from galena when heated with scrap iron. This is a process also practised in the metallurgy of lead.

3. Suppose the double chloride of cerium is $CeCl_4$, 2 NaCl, write the reaction whereby the metal may be produced according to the method of Berzelius.

CHAPTER XXII

GROUP II.—NEGATIVE SERIES: ZINC, CADMIUM, MERCURY

THIS series of elements is comprised of zinc, which was long used in its alloys (brass) before it was known; cadmium, a nearly constant impurity in zinc, which was discovered not a century ago; and mercury, the only liquid metal known, which was written about at least 300 B.C. All occur in nature as sulphides, mercuric sulphide (cinnabar) doubtless attracting attention of peoples very early, as it is bright red. Mercury is the only member of the series found free in nature. The molecules of all of them at high temperatures contain only one atom. All form oxides of the type XO, while cadmium and mercury also form an oxide of the type X_2O.

Zinc was prepared during the Middle Ages. It occurs as the sulphide (ZnS, sphalerite or zinc blende, some of which is phosphorescent), carbonate ($ZnCO_3$, calamine), silicate (Zn_2SiO_4, willemite), and the complex oxide (Fe, Zn, Mn)O, $(FeMn)_2O_3$, franklinite.

It is prepared by forming the oxide (if the ore is a sulphide, this is done by roasting) and then reducing with carbon in earthenware retorts at +1300° to +1400°. The vapor of zinc condenses to a liquid, which is cast into blocks called "spelter."

It is a bluish white, lustrous metal which is crystalline. Its malleability varies with the temperature. Ordinarily it is brittle, but when heated to from +100° to +150°, it is workable and can be rolled into sheets, hence it is rolled hot. At higher temperatures, just below the melting point, it is very brittle and readily pulverized. When zinc is distilled and the vapor suddenly cooled, a gray powder forms known as "zinc dust." It tarnishes in moist air, the tarnish forming a coat which is impervious. It decomposes water only at red heat. At high temperature it unites with oxygen with an intense greenish white light, rich in actinic rays, forming zinc oxide. When pure it is slowly attacked by acids. As it is had in commerce it dissolves readily in acids and caustic alkalies, giving off hydrogen. Zinc dust is much more reactive than the massive form. The element in dissolving in the alkalies shows its electronegative properties:

$$Zn + 2\ NaOH \rightleftarrows Na_2ZnO_2 + \uparrow H_2.$$

Zinc is used in sheet form for coating statues and in architectural adornment, in galvanic batteries, coating of iron (galvanized iron), and in the manufacture of several important alloys, as brass and argentan.

Cadmium was discovered in some impure zinc carbonate. The smoke from zinc furnaces burns with a blue to green flame and deposits a white powder. When cadmium is present it is brown. It was thought to be arsenic at first, because it forms a yellow sulphide. *Cadmia* was an early name applied to zinc ore.

It occurs chiefly with zincblende, as greenockite (CdS), and also in the carbonate. Some Silesian zinc ores carry 5 per cent. of cadmium.

It is extracted in the same way that zinc is. It is the first portion of the distilled metal.

Cadmium is a white, lustrous, fibrous metal which may be bent without a cracking noise. It is less easily soluble in dilute acids than zinc. Zinc throws it out of solution. Cadmium is used chiefly in certain alloys which fuse at low temperatures.

Mercury distilled from cinnabar was known as *hydrargyrum* (water silver). The earliest mention of *argentum vivum* (quicksilver) was about 300 B.C. It is found sometimes free in pockets, but chiefly as cinnabar (HgS), in California, Texas, Spain, and Austria.

It is prepared by roasting in the air:

$$HgS + O_2 \rightleftarrows \uparrow Hg + \uparrow SO_2.$$

Mercuric oxide, which we should suspect as being formed in the process, is decomposed at the temperature of the furnace. The essential factors in the metallurgy of mercury are ample cooling chambers to condense the vapor and provision for collecting the condensed liquid, which is readily absorbed by porous earthenware or bricks.

It is the only positive element that is a liquid at ordinary temperatures. It is an excellent conductor of heat and electricity. It is opaque and has a brilliant silvery luster. The solid crystallizes in regular octahedra. As ordinarily prepared, after straining through chamois skin, it contains small amounts of other metals. These are removed in part by treatment with various acids and then distilling under reduced pressure in contact with oxygen, which attacks such impurities as zinc. The oxides formed do not distill over (Hulett). When pure it is not affected by the atmosphere at ordinary temperatures. Just below the boiling point it forms the red oxide, HgO. It combines directly with chlorine, but is insoluble in dilute hydrochloric and cold sulphuric acids; it is soluble in dilute nitric acid. It dissolves almost all metals, especially gold, silver, tin, and sodium, forming *amalgams*.

On account of the wide range of temperature through which it remains liquid, its low vapor tension and high specific gravity, mercury is used in some barometers. A column one square inch supported by the normal pressure of the air weighs about 15 pounds. If the column has an area of one square centimeter, it weighs about one kilogram. Its uniform expansion with changes of temperature makes it suitable for use in thermometers. Its amalgamating property is utilized in making mirrors, and in the extraction of gold and silver from their ores.

Mercury forms two classes of compounds: bivalent, mercuric (HgO, $HgCl_2$), and univalent, mercurous (Hg_2O, Hg_2Cl_2). The vapor of mercury is very poisonous, and so are its compounds. The metal in quantity is nearly insoluble in animal secretions, so does not act as a poison, unless in a fine state of subdivision.

GROUP II. — NEGATIVE SERIES

ELEMENT	ZINC	CADMIUM	MERCURY
Derivation of name	German — zinn (tin) with Slavic suffix k. (Klugge)	Cadmia fornicum (furnace zinc)	Roman deity. Mercurius
Symbol	Zn	Cd	Hg
Discoverer . . .	Known in early times	Hermann, Stromeyer, independently (1817)	Known very early
Atomic weight .	65.4	112.4	200.0
Physical state . .	Solid	Solid	Liquid
Appearance . .	Bluish white, lustrous metal	White, lustrous metal	Brilliant luster
Specific gravity .	7.1	8.64	13.55
Melting point . .	+ 419°	+ 321°	− 39°
Boiling point . .	+ 940°	+ 800°	+ 357°

EXERCISES

1. Write the equation for the roasting of zincblende; also for the reduction of the oxide (ZnO) by carbon.

2. Do the same for cadmium sulphide.

CHAPTER XXIII

GROUP I.—NEGATIVE SERIES: COPPER, SILVER, GOLD

THE members of this series possess great scientific and practical interest. All occur in nature in the free condition and possess a characteristic brilliant luster. This property evidently attracted the attention of early peoples, for they were known to the ancients. All three also occur in sulphides, but with the exception of copper, not as oxides. They are soft, malleable, ductile, and the best known conductors of heat and electricity. Gold and silver are so soft that they are rarely used in the pure form, but as alloys. These alloys have served as mediums of exchange from the earliest days of bartering. The conversion of copper and silver into gold was one of the aims, if not the main ambition, that stimulated the alchemists. They are readily separated from their soluble compounds to the free condition by zinc, iron, and phosphorus. As they are little affected by the air, cooking (copper) and food vessels are made of their alloys. However, they are all poisonous in their soluble compounds. All combine directly with the halogens. Each forms two series of compounds, as illustrated by their oxides: cuprous (Cu_2O), cupric (CuO); argentous (Ag_2O), argentic (Ag_2O_2); aurous (Au_2O), auric (Au_2O_3).

Copper occurs not only as octahedral crystals in the Lake Superior region, but in important compounds, as cuprite (Cu_2O), chalcocite (Cu_2S), malachite [$CuCO_3$, $Cu(OH)_2$], azurite [$2\,CuCO_3$, $Cu(OH)_2$], chalcopyrite (Cu_2S, Fe_2S_3), and bornite ($3\,Cu_2S$, Fe_2S_3).

Silver occurs as argentite (Ag_2S), proustite (Ag_3AsS_3), pyrargyrite (Ag_3SbS_3), argyrodite ($3\,Ag_2S, GeS_2$), horn silver ($AgCl$), and in nearly all lead ores.

Gold occurs, probably as the sulphide, along with copper and iron sulphide ("sulphurets"), and as telluride, sylvanite [$(Au, Ag)Te_2$].

Metallurgical practices involving the application of engineering skill and chemical principles are often quite complicated. The winning of these three elements from their ores depends upon the form in which they occur. As all three are often present in the ore of any one of them, we may consider their extraction together, and thus secure an excellent illustration of the intricate chemical relations involved in securing the metallic elements on a commercial scale.

First, if the metal is free:

A. Copper is separated by crushing and washing the ore, then melting the metal out by heat, having added something (a *flux*) to combine with the remaining country-rock to produce a *slag*, which is a liquid at the temperature when the metal is molten. The melted copper is heavier than the slag, sinks to the bottom of the furnace, is run off from time to time, and cast in molds.

B. Silver and gold do not occur in sufficient quantity to be treated in this manner. They require some solvent to concentrate them. This solvent may form a simple or chemical solution.

I. Simple solutions of silver and gold are produced by the direct treatment with mercury, which forms an amalgam. Gravel containing free gold is a secondary formation and is usually spoken of as "placer gold." If it contains enough gold to warrant its working, it is called "pay dirt." The gravel is concentrated by *panning*, that is, it is shaken with a semi-circular jerk motion, similar to that employed in sifting meal or flour, to concentrate the heavy particles of the metals in the bottom of the "pan," "cradles," or "tables" (the form and shape of the machine depending upon the amount to be treated, method of treatment, and materials at hand). The valueless rock above is then scraped, washed, or blown off. Mercury is added, and amalgamation of the silver and gold results. Gold, especially, often occurs free in very small amounts, less than one part to the hundred thousand in quartz rock, which is worked on a large scale successfully for the extraction of its "values." This rock is usually hard and brittle. It is crushed under water in the presence of mercury by a method of *stamping*. The heavy mercury is washed free from any sand or dirt and the excess is squeezed out through chamois skin. The amalgam is then placed in an iron pot or retort and heated. The mixture of silver and gold remains behind.

II. Gold is soluble in a water solution of chlorine, bromine, or an alkaline cyanide. When the crushed ore is treated with these liquids, the silver and gold form chemical solutions, which may be drawn off. On adding zinc, or iron, ferrous sulphate ($FeSO_4$), or hydrogen sulphide, the silver and gold are precipitated from the clear solution as a brown or black mud. It is separated by filtering, and, when fused, assumes the familiar metallic appearance.

Second, when the metals occur in compounds, other procedures are followed.

A. Preliminary treatment is necessary to put the metals in the free condition before the methods given above are applicable. Usually the ore is crushed and concentrated in a current of water by shaking with various mechanical devices. The lighter valueless rock is washed away ("tailings"). The "concentrates" are roasted. Gold and silver are liberated. This material is then "amalgamated," "chlorinated," or "cyanided."

B. However, when copper ore, which usually carries some gold and silver, is roasted, copper oxide is produced. To secure the copper, a *smelting* process is pursued. The ore, which nearly always contains some iron sulphide, is partially roasted. The iron sulphide is oxidized first, FeO being produced. Siliceous matter (sand) is added, the air shut off, and the temperature raised. The iron oxide combines with the silica, forming a fusible slag ($FeSiO_8$) and floats upon the CuS, which melts and runs to the bottom of the furnace. The latter (*matte*, which contains some free copper) is run into another furnace, where, after it is two thirds roasted, the air is shut off and the reduction completed (see *lead*). This "coarse copper," which contains many impurities, as lead, arsenic, gold, silver, and so forth, is cast into ingots.

The copper is then refined electrolytically. Thin sheets of copper joined to the negative pole of a direct current are suspended in a weak acid solution of copper sulphate. Slabs of the impure copper, weighing several hundred pounds, are suspended between the thin sheets and joined to the positive terminal. In the passage of the current of 0.5 volt, or less, the copper travels from the positive to the negative pole, where it is deposited. Electrolytically refined copper is very pure. The impurities fall to the bottom of the tank, making a sludge which contains the gold and silver.

C. Most lead ores, especially galena, carry some silver, which is found in the lead obtained. Often argentiferous and auriferous ores are purposely added to lead ores in the process of smelting. The molten lead passes through the mass, dissolving the gold and silver, and collects at the bottom of the furnace. It is cast into "pigs" or run into iron pots. Molten zinc and lead are only slightly soluble in each other (less than 2 per cent). Silver is more soluble in molten zinc than in lead. When zinc is stirred in the molten lead obtained above, it dissolves the silver and floats on top. This solidifies at a temperature when the lead remains a liquid and is skimmed off. The remaining lead is practically free from silver (Parkes process).

The zinc-silver alloy contains some lead, which is finally removed by *cupellation*. In this operation, which consists in passing a blast of air over the molten metals in a cupel made of bone-ash, the lead is oxidized to litharge (PbO). This melts, some of it running over the edge of the cupel, and the rest is absorbed by the cupel. The zinc is then distilled off in clay retorts.

Third, the gold and silver are separated by boiling in nitric acid, in which the latter only is soluble (quartation), or by electrolysis. The latter method is extensively used now in the following manner: The bar of mixed metals, connected with the positive terminal of an electric circuit, is suspended in an acid solution of silver nitrate and separated by a heavy canvas partition from the negative terminal. The silver dissolves and is deposited in crystalline form upon the negative plate, while the gold is collected as a brown mud by the canvas partition. The latter is burned, the metal fused and cast into bricks. In mints the gold is again refined by electrolysis in an acid auric chloride solution to remove platinum.

The comparable properties of these elements are mentioned in the table.

GROUP I.—NEGATIVE SERIES

ELEMENT	COPPER (CUPRUM)	SILVER (ARGENTUM)	GOLD (AURUM)
Derivation of name . .	Æs Cyprium	Seolfor	Ghel (be yellow)
Symbol . .	Cu	Ag	Au
Atomic weight	63.6	107.88	197.2
Specific gravity	8.93	10.5	19.3
Appearance .	Red	White	Yellow, lustrous metal
Crystalline form	Octahedra	Octahedra	Octahedra
Melting point .	+ 1090°	+ 960°	+ 1060°
Boiling point .	+ 2100°	+ 1360°	+ 1800°
Conduct with oxygen . .	Tarnishes in moist air. If at high temperature, it burns with a green flame.	Does not combine. Absorbs 22 vols. when melted; when cooled gives it up with "sprouting"	Not affected
Soluble . .	In nitric and hydrochloric acids	Soluble in nitric acid	Insoluble in single acids. Soluble in aqua regia, which liberates free chlorine

Copper is not easily cast. In thin sheets it transmits green light. Its properties are much affected by impurities. A small fraction of a per cent of arsenic lowers its conducting power for electricity materially. It is extensively used for this purpose. It forms many useful alloys, brass (with zinc) and Dutch metal ("gold leaf"), gun and bell metal (with tin), and bronze and german silver (with tin and zinc).

Silver may be had in several allotropic forms in addition to the familiar insoluble variety: one that is soluble in water, giving it a characteristic blue color; another giving a red solution. These are colloidal solutions (*vide* Chapter XXXVI). Such solutions of metals ordinarily insoluble in water, as silver, gold, and platinum, may be made by sparking wires underneath water. Silver may be obtained as a lilac precipitate, insoluble in water, and in a form which resembles gold in color and luster (Lea). Silver is oxidized by ozone. It turns black in contact with sulphur. This is commonly spoken of as "oxidized silver." Its alloys with copper are used for coinage purposes and for making silverware.

Gold may be hammered into sheets so thin that it takes 280,000 placed one upon the other to make an inch ("gold leaf"). It is so ductile that one gram may be drawn into a wire five miles long. Its alloys with copper and silver are used for coins and to make goldware. Pure gold or pure silver is too soft to be used alone for coinage purposes. Gold is commercially measured by carats, twenty-four being pure; or by "fineness," one thousand being pure.

EXERCISES

1. Contrast the properties of the members of the positive and negative series of Group I.

2. How many ounces of gold per ton are represented by forty parts to the million? What would be the value of such ore, rating gold at $20.00 per ounce?

3. Write the reactions taking place in roasting chalcopyrite, proustite, and sylvanite. Copper forms CuO; arsenic, As_2O_3; iron, Fe_2O_3; and tellurium, TeO_2.

4. Write the reaction by which copper sulphide (CuS) may reduce the partially roasted matte to produce metallic copper.

5. How does the law of partition apply to the Parkes process for the separation of silver from lead?

CHAPTER XXIV

POSITIVE SERIES OF GROUPS V, VI, VII

GROUP V. — POSITIVE SERIES

THE three rare elements comprising this series, vanadium, columbium, and tantalum, occur in rare complex minerals. While they are distinctly metallic in character, they are always found combined with oxygen in compounds, similar to the phosphates, which show acidic properties. For instance, the minerals are vanadates, columbates, and tantalates.

Vanadium is found in the ashes of many plants, peats, and coals; in fact, widely distributed, but in very small amounts. Its compounds have been found useful in dyeing, making indelible ink, and ceramic decorating. Compounds of the other two have so far not exhibited properties which make them useful.

The elements may be prepared by the method of Berzelius or electrolysis of the fused double chlorides of the alkali metals. A recently devised method, the one now used, is very interesting. Some oxides, as magnesium oxide, when heated white hot, conduct an electric current (Nernst). These oxides break up into the metal and oxygen, but as they immediately reunite, no evidence of the dissociation is had after the current ceases to pass. If the oxides, in filament form, are treated in this manner in a vessel attached to a vacuum pump, the oxygen is drawn off and constantly removed by the pump. In time the filament becomes one of the pure metal (von Bolton). In this manner incandescent electric lamps are made containing these elements as filaments. The "tantalum lamp" consumes about one half the current required by the carbon filament, but in a 110 volt circuit, in order to get 22 candle power, it is necessary to have a filament 50 centimeters long. The filament is strung upon supporting glass prongs and presents a spider web appearance inside the bulb.

GROUP V. — POSITIVE SERIES

ELEMENT	VANADIUM	COLUMBIUM (NIOBIUM)	TANTALUM
Derivation of name . . .	The goddess Vanadis	Columbia (Niobe, daughter of Tantalus)	Mythological character, Tantalus
Symbol . . .	V	Cb (Nb)	Ta
Discoverer . .	Sefström	Hatchett	Ekeberg
Date . . .	1830	1801	1802
Element isolated by .	Roscoe (1867)	Roscoe (1877)	Berzelius (1824)
Atomic weight	51.2	93.5	181
Appearance .	Lustrous metal	Grayish black powder	White metal
Specific gravity	5.5	7.06	10.4
Melting point .	+ 1680°	+ 1950°	+ 2250°

Tantalum in its purest form [illegible] best steel with a greater [illegible] known to be possessed [illegible] to cut it with a diamond [illegible] but because it is so [illegible] small springs and [illegible] to mechanical wear.

Vanadium is [illegible] production of sheet [illegible] increases the [illegible] tempering.

G[illegible]

The elements [illegible] ative in never o[illegible] other elements. [illegible] lets by the Berzelius [illegible] alumino-thermic process [illegible] brilliantly lustrous me[illegible] at ordinary temperature [illegible] with oxygen. [illegible] make high-grade [illegible] strength, toughness and [illegible] particular uses, especially [illegible] tools and small parts of [illegible] serious [illegible] [illegible]

[illegible]

Chromium is converted into many compounds which are used for the preparation of colors, battery fluids, photographic materials, and so forth. Chromium dissolves in hydrochloric acid. When previously dipped in nitric acid, it becomes "passive" and no longer displaces hydrogen in hydrochloric acid.

Molybdenum occurs mainly as sulphide (MoS_2) and as wulfenite ($PbMoO_4$).

Molybdenum in the form of compounds is used in the laboratory. The metal, when melted, dissolves carbon and becomes so hard that it will scratch glass.

Tungsten occurs as wolframite ($FeWO_4$), scheelite ($CaWO_4$), and stolzite ($PbWO_4$).

Tungsten is used for making filaments for incandescent electric lights. "Tungsten lamps" yield the same amount of light as those with carbon filaments, but use only one quarter to a third of the current. They have a longer life, but have not been made commercially so that they may be used at all angles and to withstand the constant vibration of cars, and so forth. Its compounds are used in dyeing and to render cloth fireproof.

Uranium occurs as uraninite (U_3O_8, or $UO_2, 2\,UO_3$), and in all radio-active minerals. The latter are very complex in composition. It has the highest atomic weight of any of the accepted elements.

The compounds of uranium are used in dyeing and in making "uranium glass," which shows a yellowish green fluorescence, especially under the influence of ultra-violet light.

GROUP VI. — Positive Series

Element	Chromium	Molybdenum	Tungsten (Wolframium)	Uranium
Derivation of name. . .	Χρῶμα (color)	Μόλυβδος (lead-like appearing minerals)	Tung (heavy) + sten (stone)	Planet Uranus
Symbol. . .	Cr	Mo	W	U
Discoverer .	Vauquelin and Klaproth independently	Scheele (Hjelm isolated metal, 1782)	Scheele (d' Elhujar 1783)	Klaproth (Péligot isolated element, 1842)
Date . . .	1797	1778	1781	1789
Atomic weight	52.1	96.0	184.0	238.5
Specific gravity	6.7	8.6	19.1	18.7

Group VII. — Positive Series

Only one element is known in this series: —

Manganese, Mn, at. wt. 55, which was discovered by Bergmann (1774) and isolated by Gahn, occupies a unique position. In general physical properties it shows little or no resemblance, but certain characteristics of its compounds carry out the analogy, to the group type, chlorine. It forms no compounds with hydrogen, but several with oxygen. It bears a close resemblance in physical properties to iron in Group VIII.

Although small amounts of metallic manganese are found in meteorites, the element is found chiefly as the oxygen compounds and always contaminated with iron. The main occurrence of manganese is as pyrolusite (MnO_2), hausmannite (Mn_3O_4), braunite ($3\ Mn_2O_3$, $MnSiO_3$), manganite (Mn_2O_3, H_2O), and rhodochrosite ($MnCO_3$).

It is prepared by reducing the oxide with carbon, as iron is, and by the Goldschmidt process.

It is a hard, white, malleable metal which fuses at + 1900° and has a specific gravity of 7.2 to 8. It oxidizes very easily, "rusting" in moist air, and is readily soluble in acids. It forms a number of different salts divided into five different classes. In none of these is it univalent as are the other members of this group. It forms alloys with iron (20 to 80 per cent), ferromanganese, for example, which dissolve a large percentage of carbon and play an important part in the metallurgy of iron and steel.

EXERCISES

1. Write equations indicating the reduction of the following compounds by the alumino-thermic reaction: —

Cr_2O_3, V_2O_5, U_3O_8, Mn_3O_4.

2. From what has been learned, are you able to predict another member of the positive series of Group VII? If so, tell some of its properties.

3. Write the equations for the preparation, by the method of Berzelius, of the metals from the following halides: —

WCl_2, UCl_3, and $MnCl_2$.

CHAPTER XXV

RADIUM AND RADIO-ACTIVE PHENOMENA

Phenomenon of Radio-activity. In 1896 Becquerel observed that compounds of uranium yield a radiation which affects a photographic plate through light-proof paper (Becquerel rays) in a way somewhat similar to the X-rays. Schmidt learned that thorium compounds do the same. These two elements have the highest known atomic weights. An electroscope, when well insulated, will retain an electric charge for a long time. It is instantly discharged when exposed to the X-rays. The air is said to be "ionized" and becomes a conductor of electricity, like a copper wire. If a small amount, a fraction of a gram, of any uranium or thorium compound is brought near a charged electroscope, it is discharged also, but at a slow rate, which varies with the charge, amount of substance, distance from the instrument, and so forth. By making all the factors fixed, except the kind of compound used, and timing the rates of discharge for different compounds, we secure a method of quantitatively measuring the "radio-activity." This term was applied by Madame Curie to the phenomenon discovered by Becquerel. She proved that the radio-activity of pure uranium salts varied directly according to the percentage of that element present. Some of the uranium ores, however, were found to be four or five times as active as that compound of uranium with the highest percentage of uranium. The same was true for thorium. Therefore, that something more active than either of these must be present in the natural compounds, was the postulate which led her and her husband to the separation of salts of *radium.*

The ores in which radium occurs most abundantly, pitchblende, uraninite, and carnotite, are very complicated compounds of uranium, thorium, and other rare elements. The radium occurs in them in extremely minute amounts. During the elaborate chemical treatment for the extraction of the uranium and concentration of the radium, the course followed by the latter is readily ascertained by determining the ionizing value of the various products obtained in the process.

Concentration of Radium Compounds. The ore is pulverized, digested in boiling sulphuric acid, diluted, and filtered. Most of the uranium goes into solution, the radium remaining in the residues. We do not know the compound in which radium occurs in its ores, but this conduct indicates that it exists either in a form insoluble in sulphuric acid, or in a form which combines with the sulphuric acid to produce an insoluble sulphate. We know that radium forms an insoluble compound with sulphuric acid. The residues are then fused with sodium carbonate and leached with water. This is the common method for decomposing insoluble sulphates. The sodium sulphate produced in the fusion is dissolved by the water. The residue, carbonates insoluble in water, is then treated with hydrochloric acid, as the carbonates are decomposed and dissolved by that acid. Sulphuric acid is added to separate the alkaline-earth metals. Barium sulphate ($BaSO_4$) is very insoluble in water, and the final solution is made in hydrobromic acid. Radium bromide is less soluble in water than the corresponding compound of barium. They are separated by *fractional crystallization.**

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* When a solution containing two solutes is evaporated until crystallization begins, the excess above saturation of both solutes separates out. As the solution tension of different solids are as a rule unlike, one solute separates

Properties of Radium Compounds. Radium is known only in its compounds, the bromide, chloride, sulphate, acetate, and carbonate. Weak alloys of radium with mercury have been made, but little is known of them. When freshly prepared, the salts of radium are white and resemble similar salts of barium. In time, however, they become purple and brown. Radium shows an equivalence of 113.25 to 35.45 of chlorine. Chemically it resembles barium, which is bivalent, therefore it has an atomic weight of 226.5 (Curie, Thorpe). It possesses a characteristic spectrum, hence it is regarded as an element (*vide* Chapter II).

We are more familiar with the conduct of radium bromide ($RaBr_2$) and chloride ($RaCl_2$) than the other salts. They show remarkable photo-activity and intense ionizing power. The purest bromide shows an activity abcut 1,800,000 times that of uranium. These compounds constantly evolve heat, and in relatively enormous quantities. For instance, 1 g. evolves 100 calories per hour. The total amount of heat that may be spontaneously produced by 1 g. has been estimated to be nearly 100 billion calories, or equivalent to that produced by burning over 300 kg. of hydrogen in oxygen. The temperature of solid radium bromide is from 1° to 5° higher than the surrounding media from $-190°$ to $+450°$.

Radium salts are phosphorescent. When in contact with, or near by, certain minerals and chemical compounds, as diamonds, willemite (zinc ortho-silicate), Sidot's blende (zinc sulphide), and barium platino-cyanide, this phenome-

in greater amount, but it is always contaminated by some of the other. If a solution be made of this mixture and crystallized, a solid is obtained with a still larger proportion of that one which preponderated. By repeating the process a number of times, a very pure solid is obtained at one extreme and a very pure liquid at the other, but each contains some of the other. This process of *fractional crystallization* is one extensively practiced in chemistry.

non is most pronounced. Radium salts darken paper when in contact with it for some time; and give some glass a pink and other a brown color, depending upon the composition of the glass. Radium compounds exert physiological actions not yet thoroughly understood. It interferes with the germination of seed and retards the growth of plants. In contact with living flesh, even when confined in glass tubes, it produces acute irritation, which often results in bad sores difficult to heal. It has a destructive action upon some animal cells and stimulates others. It has been used successfully, by contact action, in the treatment of some forms of disease, as lupus and goitre.

Explanation of the Conduct of Radio-active Substances. The most acceptable explanation by which these unusual and unique properties are understood depends upon the assumption that the rays emitted by radio-active compounds consist of minute particles of two kinds. Those particles which produce the ionization effects are known as *α-particles*. They bear a charge of positive electricity, and have twice the mass of a hydrogen atom. Those particles which produce the photographic effects are called the *β-particles*. They bear a charge of negative electricity and are only about 0.001 the mass of a hydrogen atom (electrons, corpuscles). If these are screened off, by methods too complicated to explain here, rays are still obtained, *γ-rays*, which resemble the X-rays in penetrating and ionizing properties and photo-chemical effects. The γ-rays have not been found except when β-particles were present.

Emanation. Radium constantly produces a gaseous substance condensable at −150°, known as *radium emanation* (Rutherford). The amount produced is increased by heating or dissolving the soluble salts in water. The emanation is far more radio-active than radium. It is not a permanent body, but disintegrates quite readily, losing one half its activity within four days. As the emanation decays, a series of other radio-active bodies is produced, each disintegrating at a characteristic rate. Each gives off α-particles, or β-particles and γ-rays, or both, and two of the series give none of these. The emanation, having expended its energy, as it were, eventually changes, in part at least, into the final inactive element, helium. (Ramsay, Soddy.)

Life History of Radium. As the radium is disintegrating and it eventually disappears, we must account for its presence in the minerals from which it is extracted. Every uranium mineral contains radium and the emanation in proportion to the amount of uranium present. When a uranium compound is freed from radium, the emanation is slowly but regularly reformed. Therefore, it appears that uranium is the source. If we express the life of each educt in terms of the times required to decay to half value, the history of radium may be shown by a diagram as follows (Rutherford):

$$\begin{array}{cccccccccccc}
\text{U} & \rightarrow & \text{U–X} & \rightarrow & \text{Ionium} & \rightarrow & \text{Ra} & \rightarrow & \text{Emanation} & \rightarrow & \text{A} & \rightarrow \\
5\times 10^{9}\text{ yr.} & & 22\text{ da.} & & ? & & 2000\text{ yr.} & & 3.8\text{ da.} & & 3\text{ min.} & \\
\text{B} & \rightarrow & \text{C} & \rightarrow & \text{D} & \rightarrow & \text{E} & \rightarrow & \text{F} & \rightarrow & \text{G} & \\
26\text{ min.} & & 19\text{ min.} & & 40\text{ yr.} & & 6\text{ da.} & & 45\text{ da.} & & 140\text{ da.} &
\end{array}$$

The same, but not so completely, may be shown for thorium. A number of radio-active substances have been announced, as polonium, actinium, emanium, radio-lead, and so forth. Most of these have been accounted for as containing an excess of one or several of the disintegration products shown above, or in a similar diagram for thorium.

Recently Ramsay has shown that when the emanation decays in the presence of water alone, neon and not helium is produced. If the decay occurs in the presence of water containing a copper salt in solution, argon is produced. Therefore it appears that radium emanation, the most active substance known, disintegrates into one member of the family of inert gases, helium, neon, or argon, depending upon conditions. So far efforts to convert argon, neon, and helium, obtained from other sources, into each other have not been successful. Yet the transmutation of one element into another appears to have been accomplished.

EXERCISE

Harmonize the last sentence with the definitions of an atom and an element.

CHAPTER XXVI

GROUP VIII.—THE IRON METALS

THE elements arrange themselves in the eighth group in quite a different manner from that observed in the other groups. They form four periods of three elements each. In each period the elements have nearly the same atomic weight, the extremes not differing by more than five units. When arranged in the order of the increase in atomic weight, three vertical series are obtained. The members of each show striking similarity in their chemical conduct. This is not true in one case; namely, with nickel and cobalt. Their positions in the table are reversed. This constitutes an exception to the law, as all efforts so far to show a different relationship in their atomic weights have been in vain. The members of each period resemble each other in physical properties to a marked degree. We do not know enough about the gadolinite metals (samarium, europium, and gadolinium) to say definitely that they belong in this group, but from the atomic values, if the law is true in the main principle, they are properly placed in the table. The members of the first vertical series, iron, ruthenium, and osmium, are readily oxidized, whereas the others are not. In fact, many of their compounds yield the free elements on heating in the air.

THE IRON METALS

Iron, cobalt, and nickel are brilliant, lustrous, malleable, ductile metals which conduct heat and electricity. They possess properties, strength, unalterability on exposure to the air, and so forth, that make them of great commercial importance, while the chemistry of the three metals is of extreme interest. Iron alloyed with certain other metals (as nickel, molybdenum, and tungsten) acquires unusual properties of strength.

If we may draw distinctions among the elements, *iron* is the most important among the metals, and is widely distributed in nature. Fine grains of free iron are found in the coal measures of Missouri, some basalts, and on the Island of Disko. Meteorites, visitants from otherwhere, are primarily metallic iron with from 3 to 8 per cent of metallic nickel. The presence of the latter element distinguishes it from that of terrestrial origin. The chief occurrences, from which the metal is extracted, however, are the oxides: magnetite (Fe_3O_4), hematite (Fe_2O_3), limonite (brown hematite, $2\,Fe_2O_3$, $3\,H_2O$), siderite (black band ore, $FeCO_3$). It occurs also as sulphides, especially as disulphide (pyrites, FeS_2), which is an ore of sulphur. It is found in many silicates and is present as an impurity in almost all rocks. Its compounds constitute the coloring matter of most soils, vegetation, and blood of animals.

Cobalt and *Nickel* occur chiefly as the sulphides and arsenides: smaltite ($CoAs_2$), cobaltite ($CoAs_2, CoS_2$), niccolite ($NiAs$), gersdorffite (NiS_2, $NiAs_2$), pentlandite [(Ni, Fe)S]; and in certain silicates (garnierite) and other minerals, especially nickeliferous pyrrhotite.

Pure iron is prepared as a powder by heating especially purified iron oxide, or oxalate (which gives an oxide on heating), in a stream of hydrogen at a temperature of + 600°:

$$Fe_2O_3 + 3\,H_2 \rightleftarrows 2\,Fe + 3\,H_2O.$$

This dark powder, if the reduction is made at a red heat, glows on exposure to the air and burns (pyrophoric). It melts transitionally at + 1900°; and is a tolerably soft, tough metal, which may be magnetized. It may be drawn into wire through diamond dies. It rusts in moist air. Boiling water is decomposed by finely divided iron with the evolution of hydrogen. Chemically pure iron is rarely seen, although the best iron piano wire contains 99.85 per cent of the metal.

Technical iron is continuously produced on an enormous scale by smelting the ore in large blast furnaces, some yielding a thousand tons a day. The chemistry of iron and the principles involved in its extraction from its ores fill large volumes. The reactions involved are complicated. For our purposes a simplified statement will suffice.

Iron ore is essentially an oxide. It is reduced to the metallic form by heating with carbon. Coke or charcoal is used, not only for this purpose, but to produce the necessary heat by burning. The ore always contains many impurities, mainly siliceous (sandy) in nature. Siliceous matter when heated with lime forms a glass (slag) fusible at the temperature of reduction of the iron oxides. Limestone on heating yields lime, so the stone is added to "flux" away the silica. If the rocky impurities are mainly basic, that is, limestone, then sand is added to flux them.

A blast furnace is essentially a circular structure, made up of two truncated cones, the bases of the elongated one resting upon the base of the other, with a shell of metal. It is lined with a heat-resisting material, like fire brick. They are sometimes 40 m. high and 12 m. in diameter at the widest part. The top is closed by a bell which descends when a charge is added. The furnace rests upon a sandstone basin (hearth) which must be well drained. At the lowest point in the hearth is an opening for running off the molten metal. Air blasts (tuyères) are provided at the proper height above the hearth. Between the metal outlet and the air inlets is another, but smaller, opening through which the molten slag runs out continuously during the operation of the furnace. Coke, iron ore, and limestone (solids) are dumped in at the top. The last two constitute the "burden" of the charge. Air is driven in through the tuyères. The carbon burns: $C + O_2 \rightarrow CO_2$, which, coming in contact with more hot carbon, is reduced: $CO_2 + C \rightleftarrows 2\,CO$. The monoxide thus produced, on coming in contact with iron oxide, reduces it:

$$Fe_2O_3 + 3\,CO \rightleftarrows 2\,Fe + \uparrow 3\,CO_2,$$

or

$$Fe_3O_4 + 4\,CO \rightleftarrows 3\,Fe + \uparrow 4\,CO_2.$$

The carbon dioxide passes up and out of the top of the furnace. The reaction is reversible, so an excess of CO is necessary. Pure iron does not melt at the temperature it is produced (+ 500° to + 900°). It dissolves carbon, however. This it secures in part from the carbon monoxide:—

$$Fe + xCO \rightleftarrows FeCx + xO.$$

Iron which has dissolved carbon (2 to 6 per cent) melts at + 1050° to + 1250°; hence it immediately falls as drops to the hearth of the furnace, where it is tapped every six hours, run into molds of sand (cast into "pigs"), and is known as *cast iron.* The oxygen combines at once with more carbon. The lime (CaO) combines with the silica (SiO_2) to make the slag ($CaSiO_3$). The blast may be cold or hot; in the latter event, the waste hot gases are passed through "stoves" which serve to heat the air before it enters through the tuyères. Thus it will be seen that solids enter the top, and air enters the bottom. Gases are discharged from the top, and liquids drawn from the bottom.

The whole process is carefully controlled by analyses of the materials entering and products obtained. The barometric pressure and humidity of the air are also constantly noted.

Commercial iron always contains more or less carbon, which may be in the form of free graphite or combined with the iron. The presence of combined carbon (Fe_3C) is shown when iron is dissolved in hydrochloric acid by the hydrocarbons in the hydrogen evolved. Part of the odor of these gases is due to hydrogen compounds with the small amount of sulphur and phosphorus always present as impurities. There are three classes of commercial iron: (*a*) *Cast iron*, containing 2 to 6 per cent of carbon. It is brittle, but very hard; can be cast, but not welded, and can be made temporarily magnetic. Cast iron may be white, when practically all the carbon is in the combined condition. This is produced when it is chilled from the liquid state so suddenly that the carbon has no time to separate out. It is a solid solution of Fe_3C in iron. It may be gray, when all or most of the carbon is in the graphitic form. This results when time has been allowed in the cooling for the crystallization of the carbon. Cast iron also contains silicon, sometimes as much as the carbon present, a little manganese, and less sulphur and phosphorus.

(*b*) When cast iron is melted and the carbon burned away until there is less than 0.5 per cent, *wrought iron* is produced. This is accomplished by running molten cast iron, or melting pig iron, on to iron oxide mixed with a little lime in a reverberatory furnace. The mixture is stirred with iron rods ("puddled"). The carbon is burned out and escapes as monoxide; the silicon is oxidized to silica (SiO_2) and fluxes with the lime. As the iron becomes purer, it stiffens. It is removed in balls ("blooms"), and freed from the slag by rolling and hammering. Powerful machines do this work. Wrought iron is very tough, but comparatively soft; it fuses at + 1600°, or higher, according to its purity. It cannot be cast, but is easily worked with the hammer and welded when hot (+ 1000°), and is much stronger than cast iron.

(*c*) Bessemer sought to make wrought iron by bubbling air through molten cast iron to burn out the carbon, and failed. When the carbon was nearly burned out, the iron was no longer a liquid and consequently could not be poured from the vessel. After tragic experiences, he decided to stop the process at a point when the metal remained sufficiently liquid to be easily transferred. He thus discovered how to make *steel* on a tremendous scale (1856), although steel had been known for a long time. Steel contains from 0.5 to 2 per cent of carbon and possesses the advantageous properties of both cast and wrought iron. It is usually hard and possesses great strength. It can be made permanently magnetic. It may be cast and welded. If hot steel is suddenly cooled by plunging into water, it becomes very hard and comparatively brittle. If it is reheated and cooled to a definite temperature, desirable variations in hardness may be obtained. This is known as "tempering." If it is slowly cooled, it is tolerably soft and tough. This is known as "annealing." These are often combined by quickly chilling the exterior, which becomes hard, and then cooling the interior slowly, which makes it tough.

The manufacture of steel, an immense industry, as the uses of iron are widespread and important, is essentially dependent upon two processes; namely, the Bessemer ("pneumatic") and the Siemens-Martin ("open-hearth").

In the former, melted cast iron is run into a "converter" (an egg-shaped vessel lined with fire-resisting material) and air bubbled through it from the bottom. A very high temperature, sufficient to melt wrought iron with its highest percentage of carbon, is produced by the oxidation of the carbon, silicon, manganese, and some of the iron. Enough ferromanganese (which contains a large percentage of carbon) or coke is added to reduce the oxidized iron and give sufficient carbon to make the mass fusible. It is then poured off and cast into steel ingots. The Open-hearth process applies the principles involved in a different way. The cast iron is melted by playing a gas-fuel flame, an exaggerated blowpipe, as it were, in a dish-shaped furnace, lined with sand. Scrap iron and iron oxide are added in proper amounts. The heat is continued eight or ten hours, or until a test sample shows that the process is complete. The liquid steel is then drawn off and cast into ingots.

The two great enemies of steel are phosphorus and sulphur. The former makes it "cold short" and the latter "red short"; that is, the presence of those two elements, even in fractions of a per cent, makes steel brittle, when it is cold or hot, respectively. In the two processes referred to, the lining of the converter or hearth was siliceous or acidic, which facilitated the removal of sulphur. To remove phosphorus, the lining is made with a preponderance of alkaline earth metallic oxides (calcium and magnesium) and then the processes are known as "Basic Bessemer" or "Basic Open-hearth."

Iron as an electro-positive element gives two classes of salts: ferrous (bivalent, FeO) and ferric (trivalent, Fe_2O_3); as a negative element, the ferrates (FeO_3). Iron is readily soluble in acids. Galvanized iron or tin plate is made by rolling iron into thin sheets or pipes, treating with acids to remove any rust (oxide) that may have been produced and to give a perfectly clean metallic surface ("pickling"), and then passing it through molten zinc or tin, which forms a thin coating on the iron. When placed in a solution of a copper salt, iron becomes coated with copper. If the iron is previously dipped into concentrated nitric acid, washed, and then dipped into the copper solution and removed, no copper is deposited. On jarring the iron, copper at once separates from the adhering solution. The iron is said to have assumed the "passive" state. This condition may also be brought about by dipping iron into a solution of a dichromate ($K_2Cr_2O_7$, for example). Iron so treated remains exposed to the air and moisture a long time without any indication of rusting.

It is difficult to extract nickel and cobalt from the ores, as it is hard to separate them not only from the other metals but also from each other. When they are had in

ELEMENT	IRON	NICKEL	COBALT
Derivation of name . . .	Iren (īs, ice)	Kopparnickel (Kupfer-nickel)	Kobold (an evil spirit)
Symbol . . .	Fe	Ni	Co
Discoverer . .	Known to ancients	Cronstedt	Brandt
Date . . .	. . . . . .	1750	1735
Atomic weight	55.9	58.7	59.0
Appearance .	Silvery white	Bluish white	Pinkish white
Specific gravity	7.8	8.9	8.5
Melting point	+ 1550° to + 1800°	+ 1300° to + 1600°	+ 1500° to + 1800°

the form of the oxides they may be reduced with carbon: $NiO + C \rightarrow Ni + CO$; or by hydrogen: $CoO + H_2 \rightarrow Co + H_2O$. Nickel is separated from cobalt by means of carbon monoxide (Chapter XV).

While iron oxidizes most readily in moist air, or when heated in oxygen, cobalt and nickel resist the action of oxygen at ordinary temperatures, and are consequently used in plating, as in nickel plate. Nickel and cobalt plating—for the latter serves quite as well as the former—is accomplished by making an iron object the negative pole in water containing a soluble salt of nickel or cobalt, usually a cyanide. It is subsequently burnished. At high temperatures they oxidize more easily.

EXERCISES

1. Why is it necessary to have the ground upon which the hearth of a blast furnace rests well drained?

2. Why is it desirable to note the barometer and know the humidity of the air in operating a blast furnace?

3. In using "sheet tin" the presence of cracks in the tin is to be avoided. Why?

CHAPTER XXVII

THE PLATINUM METALS

THE platinum metals may be conveniently considered as *light* and *heavy*. The latter have atomic values and specific gravities nearly twice the former. As a rule, they occur native in small metallic grains in certain sands, which may carry more or less gold, especially in the Ural Mountains, Sumatra, Australia, and California. The alluvial sands are washed as in "placer" gold mining. The lustrous particles thus obtained usually contain from 50 to 60 parts of platinum, 2 of palladium, 7 iridium, 15 ruthenium, besides gold, and copper and iron compounds. The separation of these different metals is a difficult and tedious process. Platinum is obtained also from an arsenide ($PtAs_2$, sperrylite) found in Canada. Palladium is found in Brazil alloyed with gold, and in some selenium ores. It also occurs in some nickel ores (pyrrhotite) in quantities too small to be detected by the ordinary methods of chemical analysis, and accumulates in the slimes during the purification of large quantities of the extracted nickel.

THE LIGHT PLATINUM METALS

Ruthenium is steel-gray, very hard and brittle.

Rhodium is very insoluble, not being attacked by aqua regia. It is hard and difficult to fuse. When alloyed with iridium and platinum, a material is had that is very resistant to the action of chemicals, especially acids.

Palladium is a silvery white metal, which, when finely divided, dissolves in hydrochloric, sulphuric, and nitric acids. Ignited in the air it becomes dull by oxidation, but on raising the temperature it reassumes a metallic appearance. Sheet palladium absorbs, when freshly ignited, 370 volumes of hydrogen gas at ordinary temperatures, and 650 volumes at + 90° to + 100°. Palladium, when used as negative electrode in the decomposition of water, will absorb 960 times its volume of hydrogen. This would indicate the compound Pd_4H_2, or Pd_2H, but the amount of occluded hydrogen may be caused to vary with increase of pressure; that is, concentration. Therefore, the absorption of the gas by the metal appears to be a case of "solid solution." Hydrogen absorbed by palladium is more reactive than the free gas. It will precipitate copper, which is less electro-positive than hydrogen, from its salts. Free hydrogen does not do it. "Palladium sponge," made by igniting a salt, which has absorbed hydrogen, sometimes becomes heated in the air as a result of oxidation of the hydrogen to water. "Palladium black," that is, finely divided palladium, will absorb 980 volumes of hydrogen. On introducing a sheet, or sponge, of palladium into the flame of an alcohol lamp, it is covered with soot, due to the hydrogen being withdrawn from the hydrocarbons. Palladium is not used extensively in the arts.

THE HEAVY PLATINUM METALS

Osmium is the heaviest known substance. It does not fuse even at the temperature of the oxyhydrogen flame; it only sinters at about + 2500°. While it is very difficult to fuse, it is the most easily oxidized of the platinum metals. In fine powder it burns when ignited in the air to OsO_4. Incandescent lamps have been made with filaments of metallic osmium. The lack of a sufficient amount of its ores has prevented any extensive use of these lamps.

Iridium is similar in properties to rhodium, being very difficult to fuse. When alloyed with platinum it renders it quite hard.

Platinum is a soft but very tough and malleable metal which may be drawn into fine wire and hammered into foil. Below its fusing point it softens and may be welded. When it is fused it absorbs oxygen and gives it up on cooling, like silver. At ordinary temperatures platinum black absorbs 310 volumes of hydrogen. Oxygen condenses upon its surface. Platinum, when introduced into a mixture of hydrogen and oxygen, causes an explosion. This is due to the heat generated by the rapid union of that part of the gas absorbed by the metal. The gases are fully expelled at red heat. Hydrogen passes through red-hot platinum. The metal is not permeable to other gases, such as oxygen. It is not attacked readily by acids, but is soluble in chlorine water and aqua regia. Finely divided platinum ("platinum black," made by precipitating a solution of H_2PtCl_6 by zinc) does dissolve in hydrochloric acid on exposure to the air, due to its decomposition and the liberation of free chlorine. When wires of platinum, gold, or silver are held under water, and sparked by an electric discharge, the metals are converted into a colloidal form, which is soluble in water. The alkaline hydroxides, sulphides, and cyanides attack platinum at red heat. Platinum has the same coefficient of expansion as some glass. As it conducts electricity it is fused into incandescent bulbs to serve as an electrical connection between the current outside and the filament within. Platinum forms various readily fusible compounds or alloys with phosphorus, arsenic, and many of the heavy metals, as lead, hence these should not be heated in platinum vessels. But when a metal is wanted to withstand mechanical injury or chemical action, as in making standard meters, or fountain pen points, an alloy of platinum and iridium is employed. On account of its infusibility and resistance to the attacks of chemicals, platinum is used extensively in making important apparatus for the chemical laboratory and stills for the concentration of pure sulphuric acid in its manufacture. Platinum sponge serves as the "contact" material, that is, catalytic agent, in the manufacture of sulphur trioxide. The price of platinum is very high and variable. Extension of its use and fortuitous circumstances attending its extraction from its ores are the causes of this fluctuation. A heavy rainy season in the Caucasus and Russian peace increase the output with a lowering of the price.

GROUP VIII. — THE GADOLINITE METALS

ELEMENT	SAMARIUM	EUROPIUM	GADOLINIUM
Derivation of name	von Samarski	Europe	Gadolin
Symbol	Sa	Eu	Gd
Discoverer	de Boisbaudran	de Boisbaudran and Demarçay	Marignac
Date	1879	1892 and 1896	1880
Atomic weight	150.4	152.0	157.3
Appearance	Whitish-grey metal	Not yet isolated	Metal
Specific gravity	7.8	......	......
Melting point	+1300° to +1400°	......	......

EXERCISES

1. Compare the properties of the members of the three series of Group VIII. 2. How may we arrive at the formula Pd_2H?

GROUP VIII

	THE LIGHT PLATINUM METALS			THE HEAVY PLATINUM METALS		
Element	**Ruthenium**	**Rhodium**	**Palladium**	**Osmium**	**Iridium**	**Platinum**
Derivation of name	Ruthenia (Russia)	ῥόδον (rose)	Planet Pallas	ὀσμή (odor)	ἶρις (rainbow)	Platina — diminutive of plata
Symbol	Ru	Rh	Pd	Os	Ir	Pt
Discoverer	Claus	Wollaston	Wollaston	Tennant	Tennant	Unknown
Date	1844	1804	1803	1803	1803	. . . . . .
Atomic weight	101.7	102.9	106.7	190.9	193.1	195
Appearance	Steel-gray	Silvery white	Silvery white	Lustrous appearance, like zinc	Gray	Silvery white
Specific gravity	12.26	12.1	11.4	22.48	22.42	21.5
Melting point	+1800°	+2000°	+1500°	+2500°	+2200°	+1770°

CHAPTER XXVIII

HYDROGEN COMPOUNDS OF THE ELEMENTS

GROUP VII

These compounds are known as the halogen acids, and have already been considered.

GROUP VI

Hydrogen Monoxide, or *Oxygen Dihydride,* Water, has also been described.

Hydrogen Dioxide. Hydrogen forms two compounds with oxygen, — hydrogen dioxide, or peroxide, H_2O_2, being the second.

Hydrogen dioxide was first prepared by Thénard in 1818. It occurs in small quantities in the atmosphere; has been found in rain and snow; and is formed as a result of many chemical reactions. It is produced in very small quantities when a jet of burning hydrogen is cooled; but is usually prepared by treating certain metallic dioxides, as barium dioxide, with sulphuric acid: —

$$BaO_2 + H_2SO_4 \rightleftharpoons BaSO_4 + H_2O_2.$$

The reaction should be carried out in the cold.

The hydrated barium dioxide is used. This gives a water solution of the substance which is difficult to concentrate. It may be purified partially by freezing and pouring off the mother liquor, or by distilling off the water under reduced pressure.

It is a colorless, oily liquid, with sp. gr. 1.49; evaporates slowly in vacuum, and does not solidify at −30°. It has no odor, but attacks the skin when brought in contact with it, producing blisters. It is very unstable, decomposing into oxygen and water. The decomposition may take place with explosive violence. The utmost care should be exercised in opening the bottles in which the water solution is transported. The oxygen which is liberated is in the nascent condition, hence it is a powerful oxidizing agent. It bleaches organic coloring matter, liberates iodine from potassium iodide, and decomposes ozone:

$$H_2O_2 + O_3 \rightleftharpoons H_2O + 2\,O_2.$$

On account of its oxidizing property, it is used as a disinfectant. It is ordinarily used in dilute aqueous solution, "ten volume," 2.66 per cent, or "fifteen volume," 4 per cent solution. It undergoes slow decomposition at ordinary temperatures, hence the solution may be preserved only for a short time. The decomposition goes along much more rapidly in alkaline than in acid solutions. It has been used for bleaching or "blondining" the hair ("golden fluid").

Silver oxide is reduced to the metallic state by hydrogen dioxide, due to the fact that the liberated oxygen possesses a stronger attraction for the oxygen atom in the silver oxide molecule than the silver. Hydrogen dioxide is therefore a reducing as well as an oxidizing agent:

$$Ag_2O + H_2O_2 \rightleftharpoons H_2O + O_2 + 2\,Ag.$$

The graphic formula may be written thus: —

$$\begin{matrix}H\\H\end{matrix}\!>O{=}O,\ \text{or}\ H{-}O{-}O{-}H.$$

The Sulphur Hydrides. There are two of these, — H_2S and H_2S_2.

Hydrogen Sulphide, sulphuretted hydrogen, H_2S, is found in the gases of certain volcanoes, in sulphur springs, in nature as the result of the decomposition of metallic sulphides and organic matter containing sulphur. It is found in sewer gas. It may be prepared

1. By passing hydrogen over heated sulphur:

$$H_2 + S \rightleftharpoons H_2S, \text{ or}$$

2. By the action of acids upon certain sulphides:

$$FeS + H_2SO_4 \rightleftharpoons FeSO_4 + \uparrow H_2S.$$

It is a colorless gas, with an odor very disagreeable to many people, but with a sweetish taste. It dissolves in water (1 : 1.75 volumes), hence it is not collected over water. When liquefied, it boils at – 60°, and freezes to an ice-like solid at –91°. The liquid has a sp. gr. of 0.9 at –74°. It is poisonous, although not violently so.

It is much less stable than the corresponding oxygen compounds, being easily dissociated at + 400°, or slowly by the action of the oxygen of the air: $2\ H_2S + O_2 \rightleftharpoons 2\,H_2O + \downarrow 2\,S$; or at once by the halogens: $H_2S + Cl_2 \rightleftharpoons 2\ HCl + \downarrow S$. Its solution does not preserve its strength long on account of oxidation. It is slightly acid in character, and is used extensively in analyses to precipitate the insoluble metallic sulphides. The gas burns with a blue flame. If the amount of oxygen is limited, the hydrogen burns and the sulphur separates.

Hydrogen Disulphide, H_2S_2, is prepared in the same way that the dioxide is: $CaS_2 + 2\ HCl \rightleftharpoons CaCl_2 + H_2S_2$. It is a yellow, mobile liquid; decomposes into sulphur and H_2S; has a very disagreeable odor, some bleaching power, and is poisonous.

Selenium Hydride, hydrogen selenide, or selenuretted hydrogen, H_2Se. Selenium forms but one compound with hydrogen, which is a colorless gas with an odor like hydrogen sulphide, but more disagreeable and persistent. It is soluble in water, giving an acid solution.

Tellurium Hydride, hydrogen telluride, telluretted hydrogen, H_2Te, is made in the same way. It is poisonous.

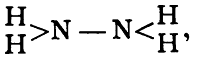
PROPERTIES OF THE HYDRIDES OF GROUP VI

COMPOUND	MOLECULAR WEIGHT	PHYSICAL STATE	SPECIFIC GRAVITY	DISSOCIATION TEMPERATURE	REACTION
H_2O	18.02	Liquid	1	+1800°	Neutral
H_2O_2	34.02	Liquid	1.5	+100°	Neutral
H_2S	34.07	Gas	1.17 (air)	+400°	Acid
H_2S_2	......	Liquid	......	Ord. temp.	Acid
H_2Se	81.2	Gas	2.81	+150°	Acid
H_2Te	129.6	Gas	4.48	Low temp.	Acid

GROUP V

The typical hydride of nitrogen, namely, ammonia, NH_3, has been considered. There are two others, however; namely, hydrazine and hydrogen trinitride. They are considered to illustrate the striking change in properties of the compounds of two elements when they are present in different proportions. Ammonia, NH_3, combines with another hydrogen to form ammonium, NH_4, which acts as a radical, forming an ammonium amalgam.

Hydrazine, diamide, N_2H_4, was separated in 1895 by Lobry de Bruyn. It may be graphically represented in this manner:



$$\begin{matrix}H\\H\end{matrix}{>}N-N{<}\begin{matrix}H\\H\end{matrix},$$

which indicates that it is NH_3, in which 1 H has been replaced by NH_2 (a radical).

It is prepared indirectly by boiling triazo-acetic acid with sulphuric acid, which gives hydrazine sulphate. This salt is decomposed by a strong base, just as ammonium sulphate is.

It is a liquid with a peculiar odor, exceedingly soluble in water, b.-p. + 113.5°; sp. gr. 1.4; stable at + 300°; very caustic, and attacks glass. It is basic and forms compounds with the acids, similar to ammonia. It is a powerful reducing agent.

Hydrazoic Acid, hydronitric acid, hydrogen trinitride, azoïmide, HN_3, was discovered in 1890 by Curtius. It is a colorless, mobile liquid at low temperatures, but ordinarily a gas possessing a very pungent, disagreeable, penetrating odor, which produces a headache. It is poisonous. The acid is unstable, decomposing with violence when the liquid is warmed. The hydrogen is replaceable by metals as in hydrochloric acid. The salts formed are very explosive.

PHOSPHORUS HYDRIDES

There are also three compounds of phosphorus and hydrogen.

Phosphine, phosphuretted hydrogen, PH_3, is prepared —

1. Reaction between calcium phosphide and hydrochloric acid, or water: —

$$Ca_3P_2 + 6\,HCl \rightleftharpoons 3\,CaCl_2 + \uparrow 2\,PH_3.$$

2. By heating phosphorus in potassium hydroxide dissolved in water: —

$$3\,KOH + 4\,P + 3\,H_2O \rightleftharpoons 3\,KH_2PO_2 + \uparrow PH_3.$$

During the reaction the air must be excluded.

It is a colorless gas, with a very disagreeable, garlic-like odor; soluble in water, and in very dilute form has a caustic taste. It ignites at + 100°, burning with oxygen to form white fumes of P_2O_5. It is easily decomposed by heat; and is very poisonous and basic like ammonia, forming compounds with the acids, as $PH_3 + HI = PH_4I$, phosphonium iodide.

Usually in preparing the gas it takes fire spontaneously on coming in contact with the air. This is due to the presence of P_2H_4.

Liquid Hydrogen Phosphide, P_2H_4, which is prepared at the same time, may be separated by carefully cooling the products as they are given off. It is a very unstable liquid; inflammable at ordinary temperatures and decomposed by slight heating, or on exposure to light, into the other two hydrides: —

$$5\,P_2H_4 \rightarrow \uparrow 6\,PH_3 + \downarrow P_4H_2.$$

Solid Hydrogen Phosphide, P_4H_2. The existence of this body is not clearly established. It seems to be a yellow powder, decomposed at $+70^\circ$; it takes fire at $+100^\circ$.

ARSENIC HYDRIDES

Arsine, arsenuretted hydrogen, AsH_3, was first observed by Scheele in 1775.

It is prepared by the action of nascent hydrogen upon compounds of arsenic: —

$$As_2O_3 + 6\,H_2 \rightarrow 3\,H_2O + \uparrow 2\,AsH_3.$$

This method of production is used in what is known as Marsh's test for arsenic.

It is a gas, m.-p. -113.5°, somewhat soluble in water, which solution decomposes on standing in the air. It burns with a blue flame, with the formation of clouds of As_2O_3. When the flame is cooled by inserting a cold object, like a piece of porcelain, the hydrogen burns, while the arsenic is deposited in the metallic form. The black deposit on the porcelain is soluble in sodium hypochlorite, insoluble in ammonium sulphide, and soluble in nitric acid, which solution after evaporation gives a red color with silver nitrate. The gas is decomposed if passed through a hot tube. It is very poisonous.

Solid Hydrogen Arsenide, As_2H_4, is a reddish brown, silky substance which is not well known.

ANTIMONY HYDRIDE

Hydrogen Antimonide, stibine, antimonuretted hydrogen, SbH_3, is prepared in the same way that arsine is and has very similar properties, being a gas with a very disagreeable odor and taste, very poisonous, and easily decomposed by heat. It burns with a greenish blue flame, with the production of white fumes, Sb_2O_3. A black deposit of metallic antimony is produced when a cold object is inserted in the burning gas, as in the case of arsine. This black deposit is insoluble in sodium hypochlorite, soluble in ammonium sulphide, and does not give the red color when treated with nitric acid and silver nitrate.

PROPERTIES OF THE HYDRIDES OF GROUP V

Compound	Mol. Wt.	Physical State	Sp. Gr.	B.-P.	Solubility in Water	Reaction
NH_3	17.02	Gas	0.59	−34°	1148 v. : 1	Str. base
N_2H_4	......	Liquid	1.003	+113.5	Sol.	Base
N_3H	......	Gas	......	−37°	Sol.	Acid
PH_3	34.02	Gas	1.18	−86°	Sol.	Base
P_2H_4	66.03	Liquid	1.01	+57°	......	......
P_4H_2	......	Solid	......	......	......	......
AsH_3	78.02	Gas	2.69	−40°	5 v. : 1	Neutral
As_2H_4	......	Solid	......	......	......	......
SbH_3	123.2	Gas	4.3	−18°	4 v. : 1	Neutral

GROUP IV

The carbon type has been discussed. Others are considered under the head of Organic Chemistry.

Two *Silicon Hydrides* are known, SiH_4 and Si_2H_6. The latter was discovered by Moissan in 1902.

Silicon Hydride, SiH_4, is prepared by treating a metallic silicide with an acid: —

$$SiMg_2 + 4\,HCl \overset{\rightarrow}{=} 2\,MgCl_2 + \uparrow SiH_4.$$

It is a colorless gas, heavier than the air, fairly stable, but decomposed at red heat. When produced with hydrogen, it is spontaneously inflammable. As a rule some free magnesium remains in the making of $SiMg_2$, so the gas takes fire as it is produced.

METALLIC HYDRIDES

There are few metallic hydrides known. They were mentioned under the elements which form them.

EXERCISES

1. In concentrating H_2O_2 by the freezing method, would the dioxide be in the mother liquor poured off or in the crystals? Give the reasons for your answer.

2. Write the equation for the production of hydrogen selenide from FeSe.

3. Write the equation for the preparation of hydrogen telluride from ZnTe.

4. Zinc arsenide (Zn_3As_2) yields arsine with hydrochloric acid. Write the reaction.

CHAPTER XXIX

HALOGEN COMPOUNDS OF THE ELEMENTS, OR HALIDES —GROUPS I, II, AND III; PHOTO-CHEMISTRY

THE halogens combine with almost all the elements, forming fluorides, chlorides, bromides, and iodides. The elements of strongly electro-positive character form the more stable compounds; for example, $NaCl$ is stable, while Cl_2O is unstable. The compounds of electro-positive elements are salts and soluble in water, with the following exceptions, namely, the chlorides, bromides, and iodides of silver; the cuprous, aurous, mercurous, thallous, lead, and platinous chlorides, bromides, and iodides; and the fluorides of copper, calcium, strontium, and barium.

The *halides* may be formed according to one or more of four type methods: —

1. By the direct union of the elements: — $Zn + Cl_2 \rightarrow ZnCl_2$.

2. By the action of the halogen acids on the metals or the metallic oxides: — $Zn + 2\,HCl \rightarrow ZnCl_2 + \uparrow H_2$;
$ZnO + 2\,HCl \rightarrow ZnCl_2 + H_2O$.

3. By the action of the halogen upon the oxide, mixed with carbon, at high temperatures: — $3\,Cl_2 + Al_2O_3 + 3\,C \rightarrow 2\,AlCl_3 + \uparrow 3\,CO$.

4. By double decomposition and the formation of the insoluble halides: — $AgNO_3 + NaCl \rightarrow NaNO_3 + \downarrow AgCl$.

Halides of Group I

Positive Series. Sodium, potassium, and ammonium fluorides are soluble, crystalline bodies which are used as fluxes. Lithium, potassium, sodium, rubidium, and cesium chlorides, bromides, and iodides are all easily soluble in water.

Sodium Chloride, common salt, NaCl, is the chief alkaline chloride and most abundant compound in which sodium and chlorine occur. It occurs: 1. In *sea-water*, which contains 3.5 per cent of solids, consisting of

Sodium Chloride ($NaCl$)	76.49 %	Potassium Chloride (KCl)	1.98 %
Magnesium Chloride ($MgCl_2$)	10.20 %	Magnesium Bromide ($MgBr_2$)	.85 %
Magnesium Sulphate ($MgSO_4$)	6.51 %	Calcium Carbonate ($CaCO_3$), etc.	
Calcium Sulphate ($CaSO_4$)	3.97 %		

Sodium chloride is obtained from sea-water or salt lakes by making salt gardens ("salt harvesting"), where the heat of the sun is utilized for concentration, which causes the separation of crystals of the less soluble constituents.

2. As *rock salt*, which is found in large deposits in Germany, Spain, Austria, and the United States, as the remnants of anciently evaporated seas or lakes. Some of it is so pure that it may be ground at once for use, but it is usually contaminated with iron oxides, clay, and sand, and requires purification. That found in New York, Pennsylvania, Kansas, California, Utah, and Louisiana is purified.

3. As *salt brines* derived from springs, lakes, and wells; that is, waters which have come in contact with beds of rock salt. The brines are evaporated by exposure in the air to the sun's heat by trickling down ricks of twigs. Large crystals, known as "solar salt," are thus obtained. Brines, as a rule, however, receive special treatment, and are evaporated by fuel heat.

Small amounts are often caught up along the seashore by the wind and carried far inland. It is present in very small amounts in almost all soils and inland waters. More than a small fraction of a per cent in the soil is injurious to vegetation. It is a constituent of most animal secretions and is necessary for animal life.

Crude salt contains several impurities, one being magnesium chloride, which attracts moisture and gives the salt a bitter taste. The "caking" of table salt is due to such impurities. Pure sodium chloride is a white substance, crystallizing in cubes, forming hats or hoppers, sp. gr. 2.13, m.-p. + 815°, volatile at a white heat. It is about equally soluble in hot and cold water; 100 parts at 0° take up 36 parts of $NaCl$; at + 100°, 39 parts. It is insoluble in alcohol. It is used in food, in making glass, glazing of pottery, and as the main source of many sodium and chlorine compounds.

Potassium Chloride is often found along with sodium chloride, though not so abundantly. It occurs as sylvite (KCl) and in carnallite ($KCl, MgCl_2, 6\,H_2O$). These impure forms are used as fertilizers and as a source of material for the preparation of potassium compounds. The chlorides are not suitable for fertilizing certain plants, as beets and tobacco. They produce a bitter taste and a slow-burning leaf.

Potassium Bromide and *Iodide* are important halogen compounds, used extensively in medicine and photography. They are usually prepared in an indirect way, as follows: bromine and iodine are allowed to act upon iron in the presence of water: —

$$Fe + I_2 \rightleftarrows FeI_2.$$

Potassium carbonate is then added to the ferrous iodide:

$$FeI_2 + K_2CO_3 \rightleftarrows \downarrow FeCO_3 + 2\,KI.$$

The solution is evaporated and the salts purified by recrystallization. One hundred parts of KI dissolve in 73.5 parts of water.

Ammonium Chloride, sal ammoniacum, NH_4Cl, may be appropriately mentioned here, as the supposititious NH_4

acts like an alkali metal. It is made largely from the ammonia water of gas works. The liquor is made alkaline and boiled. The escaping ammonia gas is absorbed in hydrochloric acid. It is a white crystalline substance, very soluble in water. When heated, ammonium chloride sublimes.

The molecular weight of a substance easily convertible into a gas is determined by measuring the volume occupied by a definite weight, when thoroughly gasified; that is, its vapor density. For example, 119 mg. of chloroform occupy 22.24 cc. when the values obtained by experiment are reduced to 0° and 760 mm. pressure. The molecular weight of chloroform ($CHCl_3$) is actually 119.5. In the case of ammonium chloride (NH_4Cl), we should expect 53.5 mg. to occupy 22.24 cc. (reduced to zero and normal pressure). In fact, experimentally we obtain twice that volume. 26.76 mg. fill 22.24 cc. When heated to + 280°, ammonium chloride begins to dissociate, and it is complete at + 380°, into free ammonia and hydrogen chloride:—

$$NH_4Cl \rightleftarrows NH_3 + HCl.$$

They recombine at once on cooling. We may now understand why the half value is obtained. 17 mg. of NH_3 ($14 + 3 = 17$) would occupy 22.24 cc.; 36.5 mg. of HCl ($1 + 35.5 = 36.5$) would occupy the same volume. If the sal ammoniac did not dissociate, 53.5 mg. ($14 + 4 + 35.5 = 53.5$) would do the same. As double the volume is occupied, two gases are produced. They may be separated when dissociated.

The dissociation of ammonium chloride is of advantage in its use in soldering. The hot iron liberates free hydrogen chloride, which attacks any adhering metallic oxide.

Negative Series. The halides of the negative series, cuprous chloride, silver chloride, and aurous chloride, as as well as the bromides and iodides, are insoluble in water. Copper, also, forms cupric chloride ($CuCl_2$), which is a blue salt, very soluble in water. Gold forms an auric chloride ($AuCl_3$), which is quite soluble and used in photography. They form many double salts, one of which is $CuCl_2$, 2 KCl, which dissolves iron. Silver chloride, bromide, or iodide is formed by precipitation. They are curdy solids, from white to yellow in color, which darken with loss of the halogen when exposed to light. Photography depends very largely upon this change.

Photography may be understood, in part, by a special case. Dry plates may be made by covering a piece of glass or celluloid with an emulsion of gelatine in which silver bromide (AgBr) is suspended. When a plate is *exposed*, although no visible alteration in the bromide is observable, it becomes apparent when it is *developed.* The silver bromide is reduced to a lower bromide (Ag_2Br) by the influence of light. The longer the exposure, which usually is only a fraction of a second, the more extended the reduction. A developer acts in the same way, reducing the silver bromide to metallic silver. Inasmuch as some of the bromide is already partially reduced by the light, the reducing agent, if allowed to remain in contact with the emulsion a limited time, completes that reduction more quickly than it reduces the unchanged bromide. In fact, the reduction of both proceeds at the same time, but one more rapidly than the other; therefore, the plate is kept in the developer only a limited time, depending upon circumstances. The most commonly used developers are alkaline solutions of the sodium salts of hydroquinone and pyrogallic acid, but we may illustrate the chemistry of the process by employing potassium ferrous oxalate [$K_2Fe(C_2O_4)_2$]. To simplify matters we make use of the ferrous, which is oxidized to ferric, oxalate in the equation, and a mixture of argentous and argentic bromide: —

$$3\,FeC_2O_4 + 2\,AgBr + Ag_2Br \rightleftarrows Fe_2(C_2O_4)_3 + FeBr_3 + 4\,Ag.$$

The unreduced silver bromide (AgBr) is then dissolved by a solution of sodium thiosulphate (commonly called "hyposulphite of soda," or "hypo"), which does not affect the metallic silver, but serves as a *fixer*. The "*negative*," on which the parts which were brightest are now opaque, and the darkest transparent, is thus produced. When the picture is *printed* from the negative, the light and dark, with their shades, are again reversed. The printing paper is coated with a silver halide emulsion which undergoes a similar treatment. In *toning*, a portion of the silver is dissolved, being displaced by gold or platinum, which is deposited in its place: —

$$NaAuCl_4 + 3\,Ag \rightarrow NaCl + 3\,AgCl + Au.$$

The thin film of the different metal gives a characteristic color or effect to the print.

Halides of Group II

Positive Series. The fluorides of the positive series are insoluble in water. *Calcium fluoride*, fluorspar, or fluorite, CaF_2, is the most important, and occurs widely distributed and is fairly abundant. Frequently it occurs in beautiful crystals, variously colored by the impurities present. It is used extensively in metallurgy as a flux, hence its name, and as a source of hydrofluoric acid. Many fluorspars possess the property of fluorescing and phosphorescing under the influence of different exciting agencies, as heat, X-rays, and Becquerel rays.

The other halogen compounds are soluble in water. Magnesium, calcium, and zinc chlorides are deliquescent.

Magnesium Chloride, $MgCl_2$, occurs in sea-water and causes the salt obtained by its evaporation to attract moisture and have a bitter taste. It is one of the constituents which give permanent hardness to waters. It is decomposed by steam, also by heat, free HCl being given off and the oxide, or an oxychloride, being formed. The anhydrous chloride may be obtained by evaporating the solution with an excess of ammonium chloride.

Calcium Chloride, $CaCl_2$, in different forms, granulated and fused, is used as a desiccating agent.

Negative Series. Zinc Chloride, $ZnCl_2$, is used as a dehydrating agent in organic chemistry, and is so powerful that it is caustic in its action upon cellulose. In the diluted form it is used as a disinfectant and in embalming fluids.

Mercury forms two chlorides: *mercuric chloride*, "bichloride," corrosive sublimate, $HgCl_2$, and *mercurous chloride*, calomel, Hg_2Cl_2. Both sublime easily. The mercuric salt fuses before sublimation. The mercurous salt is insoluble in water. It is used as a purgative in medicine. It appears to be decomposed by acids and it is regarded as dangerous to have acid or highly saline food accompany or immediately follow it, when taken as medicine, on account of the production of mercuric chloride, which is a poison. Mercuric chloride is fairly soluble in water, more soluble in an ammonium chloride solution. It is soluble in alcohol and ether, which is unusual for metallic salts. It is a powerful germicide and is used in medicine as an antiseptic, in solution 1 : 1000 or 1 : 2000.

Mercury also forms two iodine compounds: mercuric iodide, HgI_2 (red), and mercurous iodide, HgI (yellow). The former is insoluble in water, but readily soluble in a solution of potassium iodide, forming a double iodide, ($HgI_2, 2\,KI$), which is a more efficient germicide than mercuric chloride.

Halides of Group III

Boron Fluoride, BF_3, illustrates the type. Boron chloride, BCl_3, is a colorless liquid, readily decomposed in water with the formation of hydrogen chloride and boric acid: —

$$BCl_3 + 3\,H_2O \underline{\rightarrow} \uparrow 3\,HCl + \downarrow B(OH)_3.$$

Aluminum Chloride, $AlCl_3$, is a white crystalline solid which is very deliquescent. It forms double chlorides with the alkaline chlorides, and is used in the preparation of aluminum. It is used in preparing many carbon compounds. On evaporating a solution of aluminum chloride in water, it is decomposed: —

$$AlCl_3 + 3\,HOH \underline{\rightarrow} 3\,HCl + \downarrow Al(OH)_3.$$

The other members of this group also form the type, MCl_3, M standing for any member of the group. They do not decompose as readily with water. Thallium also forms another chloride, $TlCl$, which is insoluble in water.

EXERCISES

1. Why do we use the volume 22.24 cc. for milligrams in weight in determining the molecular weight of a substance by its vapor density?

2. One hundred parts of water dissolve 33 parts of ammonium chloride at 0°, and 73 parts at 100°. Suppose we had a saturated water solution of a mixture of sodium and ammonium chlorides and cooled it to zero, which would separate out, or if both, in what proportion?

CHAPTER XXX

HALOGEN COMPOUNDS OF THE ELEMENTS, OR HALIDES. — GROUPS IV, V, VI, VII, AND VIII

GROUP IV

Positive Series

Carbon Tetrachloride. Carbon does not readily combine with the halogens; but several compounds have been made by the action of chlorine upon the hydrocarbons: —

$$CH_4 + 4\,Cl_2 \rightarrow 4\,HCl + CCl_4 \text{ (tetrachlormethane).}$$

This is also prepared by the treatment of carbon disulphide with chlorine. It is distinguished from the hydrogen compounds by not burning readily. It is a liquid, sp. gr. 1.63, which boils at + 78°. It is an excellent solvent for many organic substances.

The halogen compounds are insoluble liquids in the case of chlorides, and solids in the case of bromides and iodides. At + 200° carbon tetrachloride is decomposed by water: —

$$CCl_4 + 2\,H_2O \rightarrow 4\,HCl + CO_2.$$

Silicon Tetrachloride is formed by the action of chlorine upon amorphous silicon, or a heated mixture of silica and carbon, or magnesium silicide (Mg_2Si). It is a strongly fuming liquid that is decomposed at once by water: —

$$SiCl_4 + 4\,H_2O \rightarrow 4\,HCl + \downarrow Si(OH)_4.$$

Silicon Tetrafluoride, SiF_4, is formed by the action of hydrofluoric acid upon silica: —

$$4\,HF + SiO_2 \rightarrow 2\,H_2O + \uparrow SiF_4.$$

It is a heavy, colorless gas, sp. gr. 3.07. This in turn reacts with water: —

$$SiF_4 + 4\,H_2O \rightarrow 4\,HF + \downarrow Si(OH)_4,$$
$$\text{or } 3\,SiF_4 + 4\,H_2O \rightarrow \downarrow Si(OH)_4 + 2\,H_2SiF_6$$

(hydrofluorsilicic acid, or hydrogen silico-fluoride). The latter is an unstable acid, forming a series of stable salts known as fluor-silicates. Silicon tetrafluoride is a by-product in the manufacture of phosphatic fertilizers when fluorides are present in the phosphate rock used.

Titanium Tetrachloride is a liquid which is decomposed by water to the oxychloride: — $TiCl_4 + H_2O \rightarrow \uparrow 2\,HCl + TiOCl_2$. Titanium tetrachloride, by reduction, forms a *trichloride*, $TiCl_3$, a powerful reducing agent, which readily absorbs oxygen. It is used in making coal tar colors.

Zirconium and *Thorium* form tetra- and oxyhalides which are white crystalline bodies.

Negative Series

Tin dissolves in hydrochloric acid to form *stannous chloride*: — $Sn + 2\,HCl \rightarrow SnCl_2 + \uparrow H_2$. By the action of chlorine on metallic tin, *stannic chloride*, or tin tetrachloride, $SnCl_4$, is formed. Stannous chloride is a solid, soluble in water, but quickly decomposed into insoluble stannous oxychloride and hydrochloric acid. It is a strong reducing agent. Stannic chloride is a fuming liquid which combines with three parts of water with "hissing," producing a white crystalline solid, soluble in water. It is decomposed either by heat or on allowing it to stand at ordinary temperature: — $SnCl_4 + 4\,H_2O \rightarrow \uparrow 4\,HCl + H_2O + SnO(OH)_2$ (metastannic acid).

Lead Chloride, $PbCl_2$, is formed by the action of a soluble chloride upon any soluble salt of lead:

$$Pb(NO_3)_2 + 2\,NaCl \rightarrow 2\,NaNO_3 + \downarrow PbCl_2.$$

It is only slightly soluble in cold water. It dissolves in hot water and crystallizes on cooling.

Lead Tetrachloride, $PbCl_4$, is said to be formed when lead dioxide (PbO_2) is dissolved in very cold hydrochloric acid. It is unstable, being decomposed by heat or solution in water to $PbCl_2 + Cl_2$; consequently, lead dioxide when treated with hydrogen chloride yields free chlorine: —

$$PbO_2 + 4\,HCl \rightleftarrows \downarrow PbCl_2 + 2\,H_2O + \uparrow Cl_2.$$

Lead Iodide, PbI_2, is formed in the same way that $PbCl_2$ is, but is less soluble. It is a brilliant yellow substance which crystallizes from hot water in golden scales.

Halides of Group V

The halogen compounds of nitrogen are among the most unstable compounds known. When chlorine acts upon an excess of ammonia, nitrogen is liberated. If, however, an excess of chlorine is allowed to act upon ammonia, ***nitrogen trichloride***, NCl_3, is formed. It is an oily liquid which explodes with great violence on slight elevation of temperature or the least shock.

Nitrogen Iodide [NI_3 (?), more likely $N_2H_3I_3$, or NI_3, NH_3]. When iodine is allowed to act upon strong ammonium hydroxide, a grayish black compound, containing nitrogen, hydrogen, and iodine, called nitrogen iodide, is formed. This dark body may be filtered off and allowed to dry spontaneously. When dry, the slightest touch will suffice to explode it; when moist, it gradually decomposes.

Phosphorus, *Arsenic*, *Antimony*, and *Bismuth* unite with chlorine to form trichlorides: PCl_3, $AsCl_3$, $SbCl_3$, $BiCl_3$. Phosphorus and arsenic trichlorides are liquids; the others are solids. Antimony and bismuth trichlorides, on account of their soft consistency and easy fusibility, were known to the alchemists as "butter of antimony" and "butter of bismuth." On adding an excess of chlorine, PCl_5, $AsCl_5$ (unstable above $-30°$ C.), and $SbCl_5$ are formed. Phosphorus pentachloride is a white solid. Antimony pentachloride is a liquid.

These are all decomposod by water, according to the following reactions:—

$PCl_3 + H_2O \rightleftarrows POCl$ (phosphorous oxychloride) $+ 2\ HCl$,
$AsCl_3 + H_2O \rightleftarrows AsOCl$ (arsenious oxychloride) $+ 2\ HCl$,
$BiCl_3 + H_2O \rightleftarrows BiOCl$ (bismuth oxychloride) $+ 2\ HCl$.

Phosphorus trichloride and pentachloride, as well as oxychloride, with excess of water are completely decomposed:—

$PCl_3 + 3\ H_2O \rightleftarrows 3\ HCl + P(OH)_3$ (phosphorous acid),
$PCl_5 + H_2O \rightleftarrows 2\ HCl + POCl_3$ (phosphoric oxychloride),
$POCl_3 + 3\ H_2O \rightleftarrows 3\ HCl + PO(OH)_3$ (orthophosphoric acid),
$PCl_5 + 4\ H_2O \rightleftarrows 5\ HCl + PO(OH)_3$.

The oxychlorides of antimony and bismuth are insoluble in water. They are held in solution in water by the presence of much free hydrochloric acid. Tartaric acid and sodium chloride also prevent antimony oxychloride from precipitating when water is added.

Halides of Group VI

The oxygen halides will be considered under the head of the oxides.

Sulphur Chlorides. When chlorine is led into melted sulphur, S_2Cl_2, a heavy, yellowish red liquid is formed. It is a solvent for sulphur, and the solution is used in vulcanizing rubber. When chlorine is led into S_2Cl_2 at a moderately low temperature, $+6°$ to $+8°$, SCl_2 is formed;

when chlorine is led into this at − 20°, SCl_4 is formed. These two, also, are liquids.

With the members of the positive series of this group chlorine unites directly, and several compounds are formed with each element which do not require further consideration. They are as follows: —

$CrCl_2$	$CrCl_3$	——	——	——
——	$MoCl_3$	$MoCl_4$	$MoCl_5$	——
WCl_2	——	WCl_4	WCl_5	WCl_6
——	UCl_3	UCl_4	UCl_5	——

Halides of Group VII

The halogens form several unstable compounds by direct union with each other; namely, ClBr, ClI, and ICl_3.

With manganese the halogens form compounds according to the type MnX_2. It is barely possible that $MnCl_4$ may exist at low temperatures. The manganese halides resemble the negative series of Group II.

Halides of Group VIII

$FeCl_2$	$FeCl_3$	——	$CoCl_2$	——	——	$NiCl_2$	— —	——
$RuCl_2$	$RuCl_3$	——	$RhCl_2$	——	——	$PdCl_2$	——	$PdCl_4$
——	$SmCl_3$	——	——	$EuCl_3$	——	——	$GdCl_3$	——
$OsCl_2$	$OsCl_3$	$OsCl_4$	$IrCl_2$	——	$IrCl_4$	$PtCl_2$	——	$PtCl_4$

All are made by General Methods I and II.

Nickel and cobalt act only as bivalent elements with the halogens, giving $NiCl_2$ (green) and $CoCl_2$ (rose). *Nickel Chloride,* $NiCl_2$, usually crystallizes with 6 H_2O; it loses its water on heating and becomes yellow. *Cobalt Chloride,* $CoCl_2$, combines with 6 H_2O, giving monoclinic crystals. When it becomes anhydrous it is blue in color. Characters made with this solution on paper are almost invisible, but become distinct when warmed. The solution is therefore used for one kind of "sympathetic ink."

Ferrous Chloride crystallizes from aqueous solution in green, monoclinic crystals which become brown, due to deliquescing and oxidizing in the air. The anhydrous preparation is made by passing HCl over heated iron. It is a white mass which may be sublimed at a red heat. It absorbs chlorine and is at once converted into *ferric chloride* ($FeCl_3$ or Fe_2Cl_6), a yellow, crystalline mass, very soluble in water, alcohol, and ether, b.-p. $+200°$. Vapor density determinations at $+320$ to $+420°$ indicate that the formula Fe_2Cl_6 is correct; at $+750$ to $+1050°$, $FeCl_3$.

Palladium Chloride is a brown, deliquescent mass which forms a double salt, K_2PdCl_4. *Palladium Iodide*, PdI_2, is a black mass, insoluble in water, while the chlorides and bromides are soluble in water. *Palladic Chloride*, $PdCl_4$, or hydrochlor-palladic acid, H_2PdCl_6, is formed when the metal is dissolved in aqua regia.

Platinous Chloride, $PtCl_2$, is a green powder, insoluble in water. It is obtained by heating platinum tetrachloride, $PtCl_4$ to $+200°$. It forms double salts, as K_2PtCl_4. *Platinic Chloride*, $PtCl_4$, or hydrochlor-platinic acid, H_2PtCl_6, is obtained in a similar manner. It crystallizes with six molecules of water in brown-red prisms. The chlor-platinates give a series of double crystalline salts, of which $PtCl_4, 2\,KCl$ is an example.

Ruthenium Trichloride, $RuCl_3$, when oxidized by nitric acid, forms $RuCl_3NO$, and not $RuCl_4$.

EXERCISES

1. Tabulate the chlorides, and their properties, of Group IV.
2. Write the reactions resulting from adding water to phosphorous tri-iodide; tri-bromide; antimony pentachloride.
3. How may ferric chloride be converted into ferrous chloride?

CHAPTER XXXI

DETERMINATION OF MOLECULAR WEIGHTS

In learning the composition of water, the first compound studied in this book (Chap. V), we found that the third desirable thing to know of a compound is the molecular weight of the body. The determination of the molecular weight is closely associated with the atomic weight, and is often necessary in settling upon the correct figure to be used for the latter. We know of no one method by which molecular weights of all classes of substances may be determined. Furthermore, we know no method applicable to classes of substances which has not exceptions. By a combination of methods, however, a great amount of substantial information has been accumulated. Extended study is necessary to acquire familiarity with the various methods that are used. A few typical methods will be discussed here and they are presented free from details.

1. If the substance is readily convertible into a gas, we found that the molecular weight might be obtained with ease (Chaps. VIII and IX). Many substances are not easily converted into gases, and we require other methods for determining the molecular weights than that depending upon measuring the volume occupied by a known weight of gasified substance. Furthermore, there are some substances which, on being converted into a gas, occupy a larger volume than most substances. Ammonium chloride (NH_4Cl) is an example. When it is converted into a gas, it is no longer NH_4Cl, but has been *dissociated* into two gases, NH_3 and HCl (Chap. XXIX). Each requires its

definite volume for the particular temperature and pressure. This apparently exceptional case illustrates a most important phenomenon, and offers a key to the explanation of anomalous cases arising with certain other methods which are used in determining the molecular weights.

2. The fact that substances dissolve in a liquid is one of the most familiar phenomena of nature — one of the most difficult for which to secure a satisfactory and comprehensive explanation. The term "solution" is usually applied to liquids which have dissolved a gas, a solid, or another liquid, but this is a limited application. We have learned that gases mingle with each other with perfect freedom when there is no chemical union. One gas dissolves another, as it were. One liquid dissolves another, as alcohol and water. One solid dissolves another, as shown by Roberts-Austen, who placed disks of pure gold in contact with pure lead; after four years he found that the gold had penetrated the lead. A solid may dissolve a gas, as noted in the absorption of hydrogen by palladium hydride. A gas may dissolve a liquid, as we know from the phenomenon of evaporation. A gas may dissolve a solid, as we know from the phenomenon of sublimation. These facts have been explained on the ground that molecules possess kinetic energy.

The diffusion of particles of one gas into another, assuming no chemical action, is fairly rapid. If a wall of unglazed porcelain separates the gases, the diffusion is quite rapid. If alcohol, which mixes with water in all proportions when stirred, is carefully superposed upon water, the mixing proceeds, but quite slowly. This may be shown by dropping a piece of paraffine into the upper layer of alcohol. Paraffine is heavier than alcohol and lighter than water. It therefore sinks through the alcohol until it reaches that mixture of alcohol and water which has the same specific gravity as the paraffine. When the liquids are not disturbed, the paraffine remains in nearly the same position for months.

If, however, we separate the alcohol and water by a partition made of parchment (Abbé Nollet, eighteenth century), we observe a comparatively rapid diffusion of the liquids. This phenomenon is known as *osmosis*. Nollet poured ordinary alcohol into a glass tube, the lower end of which was covered with animal parchment, that is, a bladder, and placed the tube in a vessel of water, inserting it until the two liquids stood at the same level. The liquid within the tube rose apparently contrary to the law of gravity. Pressure, *osmotic pressure*, was produced.

Bladders were found to be distensible and not sufficiently rigid for quantitative measurement. Traube, finding that certain precipitates possess the property of allowing a liquid to pass through them, devised an artificial membrane. It was learned that these membranes, when suitably deposited, allow the solvent to pass through but hold the solute back. They were designated semi-permeable. Pfeffer, a botanist, perfected these as follows: a fine-grained unglazed porcelain cup was filled with a solution of potassium ferrocyanide and then immersed in a solution of copper sulphate. When these two liquids are brought together a chocolate-colored precipitate of copper ferrocyanide is produced according to the equation,

$$2\,CuSO_4 + K_4Fe(CN)_6 \rightleftarrows \downarrow Cu_2Fe(CN)_6 + 2\,K_2SO_4.$$

Each solution will pass through the pores of the cell, carrying the solute with it. When they come together the precipitate is produced right in the walls and may be seen as a fine line when the cell is broken. The precipitated copper ferrocyanide then acts as a semi-permeable membrane.

Pfeffer found that when a solution of glucose ($C_6H_{12}O_6$) was placed in such a cell as described and submerged in water, the water rose within the cell. Morse has been able to cause the solution within to rise as high as 66 feet above the surface of the water without.

The osmotic pressures of many substances have been determined. It has been learned that if the molecular weight of a substance (in grams) is dissolved in one liter of water, it exerts an osmotic pressure equal to 22.24 atmospheres; for example, 342 g. of cane sugar ($C_{12}H_{22}O_{11} = 342$) or 60 g. of urea ($CON_2H_4 = 60$) dissolved in one liter of water at 0° exert that pressure. Or, if the molecular weight of the substance is dissolved in 22.24 l. of water, the osmotic pressure is equal to one atmosphere. Only round figures are used here.

Molecular weights (in grams) of gases occupy the same volume under similar conditions of temperature and pressure (Chap. VIII). That is to say, 2 g. of hydrogen (H_2), 17 g. of ammonia (NH_3), and 44 g. of carbon dioxide (CO_2), each occupy the same volume. If the pressure exerted by the gas particles upon the restraining walls of the vessel is equal to one atmosphere, that is, if the gases are measured under 760 mm. pressure, it is found that these molecular weights of gases occupy 22.24 l at 0°. If the pressure is increased sufficiently to cause each gas to occupy just one liter, it is found that a pressure equal to 22.24 atmospheres at 0° is necessary (Law of Boyle and Mariotte). This pressure we have learned varies with the temperature (Law of Gay-Lussac and Charles).

Van't Hoff determined that equal volumes of molar solutions exert the same osmotic pressure at the same temperature, and that the pressure varies with the temperature in the same way that it does with gases. Equal volumes of gases under similar conditions of temperature and pressure have an equal number of molecules (Avogadro). Therefore, the pressure which a gas exerts at a given temperature, if a definite number of molecules is contained in a definite volume, is equal to the osmotic pressure which is produced by this same number of molecules of *most* substances under the same conditions, if they are dissolved in any given liquid (Arrhenius' statement of the Law of van't Hoff).

To determine the molecular weight of a substance, therefore, we may take 22.24 l. of water, if that is its solvent, and add the substance to it until we find that it exerts an osmotic pressure equal to one atmosphere. The number of grams of the solute added is equal to the molecular weight. It has been learned, however, that certain substances, as hydrochloric acid, sodium hydroxide, and sodium chloride, types of acids, bases, and salts, do not obey the law, but exert a pressure of nearly two atmospheres. Hence, the word "*most*" in the statement of the law. The pressure exerted by these three classes of substances is of the same order, however.

3. If we dissolve a solid in water, the boiling point of the water is raised and the freezing point is lowered. If we dissolve 342 g. of sugar or 60 g. of urea in 1000 cc. of water, the boiling point of each solution is 100.52° instead of 100°; and the freezing point is not zero, but − 1.86° C. Equimolecular weights of non-volatile substances in solution produce the same elevation of the boiling point of the solution or the same lowering of the freezing point (Law of Raoult).

Therefore, if we desire to determine the molecular weight of a solid, we add enough to one liter of water to cause the boiling point to rise 0.52° or the freezing point to be lowered 1.86°. The amount added in grams corresponds to the molecular weight. However, van't Hoff and others learned by experiment that certain substances, acids, bases, and salts, when dissolved in water, do not give the same constant elevation of the boiling or lowering of the freezing point as generally observed, but figures approximately twice, thrice, or multiplicatively as great. These exceptional classes of substances give concordant figures among themselves. That is to say, HCl, HBr, $NaOH$, KOH, $NaCl$, and KI give double values; H_2S, $Ca(OH)_2$, $BaCl_2$ give triple values; and so on. We shall endeavor to learn in the next chapter in what way they differ from other substances in solution.

EXERCISES

1. In determining the atomic weight of oxygen, how was the determination of the molecular weight of water important?

2. How many grams of sodium chloride dissolved in a liter of water would be required to elevate the boiling point of the solution 0.52°?

3. How many grams of KI dissolved in a liter of water are necessary to lower the freezing point of the solution 1.86°?

CHAPTER XXXII

THEORY OF ELECTROLYTIC DISSOCIATION

SUBSTANCES which conduct an electric current, as copper, platinum, graphite, and charcoal, are called *conductors.* Glass, porcelain, rubber, and solid sodium chloride, which do not conduct the current under ordinary conditions, belong to a class called *non-conductors.* If the terminals of an electric current are placed in pure water or alcohol, there is no appreciable flow of electricity. They are also non-conductors. In fact, with a few exceptions, all solid non-metallic substances, as well as all pure liquids and gases, are non-conductors of electricity at ordinary temperatures and pressures. If sugar or urea is dissolved in pure water, the current does not flow through the solution. However, if a little acid, or alkaline hydroxide, or a soluble salt, is added to water, the current passes. Such solutions are conductors. The passage of the current, however, is accompanied by a decomposition of the solute. They constitute, therefore, a special kind of conductors, namely, *electrolytic conductors*, and are called *electrolytes.* The process was termed *electrolysis* by Faraday, who learned two very important facts in regard to the phenomenon; namely: —

First, *the amount of a substance decomposed by an electric current is proportional to the amount of electricity which passes through;* and

Second, *if the same current passes through several electrolytes, the amounts of the different substances separated from* *the compounds are proportional to the chemical equivalents of the substances separated.*

The latter principle may become clearer by illustration. If we have a series of electrolytes, as HCl, $NaCl$, $CuCl$, $CuCl_2$, $SnCl_2$, and $SnCl_4$, so arranged that the same current passes through each, we obtain for each gram of H, 35.45 g. Cl, 63.6 g. Cu^{I}, 31.8 g. Cu^{II}, 59.5 g. Sn^{II}, and 29.75 g. Sn^{IV}. The equivalence is based on hydrogen, or chlorine, which has the same valence.

If we suspend two pieces of platinum connected to the terminals of a direct current in a solution of copper sulphate, we observe the deposition of copper upon the negative pole and that the blue color of the solution disappears. The copper has traveled from all portions of the solution and has accumulated at one place. Faraday called these moving particles *ions* (wanderers); those going toward the anode (positive pole) were termed *anions;* those moving toward the cathode (negative pole), *cations.*

$$\text{Cations}\left\{\begin{matrix} \text{H Cl} \\ \text{K OH} \\ \text{K Cl} \end{matrix}\right\}\text{Anions}$$

The facts referred to in the last chapter, — namely, that molar solutions of three classes of substances (acids, bases, and salts) show abnormal elevation of the boiling point or lowering of the freezing point, and exert an abnormal osmotic pressure, and as that pressure is analogous to gaseous pressure, and that gasified bodies which show abnormal pressures (ammonium chloride) are dissociated into two or more gases, — caused van't Hoff to suggest that these particular substances in solution are decomposed into simpler entities, each of which has its influence. In short, sodium chloride ($NaCl$) exists in solution as sodium

(Na) and chlorine (Cl). But we have learned that both of these elements in the free condition in the presence of water decompose it, hydrogen being evolved when sodium comes in contact with water and oxygen when water is treated with chlorine. Yet we know that neither of these gases is given off when common salt (NaCl) is dissolved in water. Arrhenius (1887) offered an explanation of the statements made above in the *Theory of Electrolytic Dissociation* which now has wide acceptance. This theory assumes that when sodium chloride is dissolved in water, it is dissociated into sodium and chlorine, which do not exhibit their normal properties of decomposing water, because each carries a charge of electricity which prevents it. An ion is therefore an atom loaded with a charge of electricity. As compound radicals resemble the atoms, the same is true for them; that is, a solution of ammonium nitrate (NH_4NO_3) in water may be regarded as free NH_4 and NO_3 bearing charges of electricity.

When the current is started through a solution of an electrolyte, the charge is removed from the atom, which at once exhibits the properties we are accustomed to associate with it. If we pass a current through a dilute solution of HCl, NaOH, or NaCl in water, we obtain H at the cathode and O at the anode in all three instances. In the case of HCl, chlorine is liberated, which decomposes water, freeing O and reforming HCl, which is again decomposed and reformed. In the case of NaOH, sodium is liberated, which at once attacks the water, freeing hydrogen and reforming NaOH. Hydrogen dioxide is probably formed, and then decomposed into water and oxygen at the anode. In the case of NaCl, the Na, when freed from its charge, liberates H and forms NaOH, while the Cl liberates O and forms HCl. By separating the terminals with a porous partition, we may show that the liquid around the anode becomes acid, and that around the cathode basic. If there is no partition, HCl and NaOH combine to form H_2O and NaCl, the latter again dissociating, and so on over again.

The movement of the ions, which is thus demonstrable, is sluggish, but the charge borne by each ion is very large. The electric current sufficient to deposit 31.8 g. of copper (Cu^I) will keep a 50-candle-power incandescent lamp glowing for 13.5 hours. If condensed upon metallic spheres held a meter apart, the charge would exert an attraction equal to a force of 10^{16} tons.

The cause of this phenomenon of "ionization" is not fully understood, but doubtless certain solvents possess some specific power which separates the molecules into ions. The power of solutions of electrolytes to conduct the current increases with dilution. Water is the best dissociant. When the solution of HCl in water is concentrated and electrolyzed, we obtain H and Cl, but no O. Pure liquid HCl does not conduct the current. On adding a trace of water, however, the current flows. Evidently the HCl is then the solvent and H_2O the electrolyte.

The theory has been most useful in explaining many chemical reactions. For instance, a solution of sodium hydroxide may be looked upon as Na^+ and OH^- * distributed in a water medium; hydrogen chloride as H^+ and Cl^-; sodium chloride as Na^+ and Cl^-. The anion $(OH)^-$ turns a litmus solution blue; the cation H^+ turns it red. In NaCl formed from Na^+OH^- and H^+Cl^-, the anion $[(OH)^-]$

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* An ion is indicated by the small plus or minus sign at the upper right-hand corner, the former meaning a cation and the latter an anion. Univalent atoms, those carrying one unit charge, have the single sign; divalent atoms have double signs; and so forth.

and cation (H^+) have combined and no longer exist, while the Na and Cl neutralize each other, so that a solution of salt does not affect the color of a litmus solution.

Another illustration may be given. Sodium chloride in a water solution is dissociated, as noted above. A solution of silver nitrate ($AgNO_3$) is an electrolyte, being dissociated into Ag^+ and NO_3^-. If these solutions are mixed, Ag^+ and Cl^- combine to form an insoluble compound, AgCl, which separates from the medium as a precipitate. Na^+ and NO_3^- are left in the solution. Attention is to be directed here to the fact that chloroform (CCl_3H), a liquid which contains Cl in abundance, does not conduct the current; hence it is not an electrolyte. If this is mixed with a silver nitrate solution, no precipitate is formed. This indicates that chemical reactions at ordinary temperatures are facilitated by ionization.

We may take finally an illustration which involves a gas. Aqueous solutions of sulphuric acid (H_2SO_4) and sodium carbonate (Na_2CO_3) are indicated, when ionized, respectively as follows: $2\,H^+ + SO_4^{--}$ and $2\,Na^+ + CO_3^{--}$. When the solutions neutralize each other, we have $2\,Na^+ + SO_4^{--}$ in solution. Carbonic acid (H_2CO_3) is not a stable body, but decomposes into H_2O and CO_2. The latter is a gas and escapes from the solvent medium.

EXERCISES

1. Write formulas showing what is believed to take place when a direct current is passed through weak HCl, NaOH, and NaCl solutions.

2. Suppose the same current passes through solutions of the compounds enumerated below, how many grams of each metal should separate theoretically for each gram of hydrogen: —

HCl, $NiCl_2$, $FeCl_2$, Fe_2Cl_6, AuCl, $AuCl_3$, $PtCl_2$, $PtCl_4$, and $SbCl_3$?

CHAPTER XXXIII

OXIDES, SULPHIDES, HYDROXIDES, HYDROSULPHIDES

Oxides

Members of the positive series of the sixth group do not form binary compounds with the positive elements, but do with the negative elements. Oxygen forms compounds, *oxides*, with all the elements, except the "noble gases" and fluorine. The oxides of bromine have not been obtained in the pure state. With many of the elements oxygen forms more than one oxide. The oxides of the positive elements are insoluble in water, except those of the alkalies and alkaline earths, and these undergo changes before solution (hydroxides). The oxides of the negative elements generally combine with water.

Closely related to the oxides is a class of compounds containing hydrogen and oxygen, called *hydroxides*, as $NaOH$, $Ca(OH)_2$, $Fe(OH)_3$, $Zr(OH)_4$, and so forth.

General methods for the formation of the oxides.

1. By heating the element or compound in the air or oxygen: —

$$Cu + O \xrightarrow{} CuO, \quad 4\,P + 5\,O_2 \xrightarrow{} 2\,P_2O_5;$$

and $$2\,ZnS + 3\,O_2 = 2\,ZnO + \uparrow 2\,SO_2,$$

and $$As_2S_3 + 9\,O = As_2O_3 + \uparrow 3\,SO_2.$$

2. By heating hydroxides or certain salts: —

$$Cu(OH)_2 = CuO + H_2O; \; CaCO_3 = CaO + \uparrow CO_2;$$
$$2\,B(OH)_3 = B_2O_3 + 3\,H_2O.$$

HYDROXIDES

The hydroxides may be formed, —

1. By adding water to the oxide: —

$CaO + H_2O \underline{\rightarrow} Ca(OH)_2$; $P_2O_3 + 3\ H_2O = 2\ P(OH)_3$.

2. By the decomposition of water by means of a very positive element: —

$$2\ Na + 2\ H_2O = \uparrow H_2 + 2\ NaOH.$$

3. By double decomposition, whereby an insoluble hydroxide is formed: —

$$FeCl_3 + 3\ NaOH = 3\ NaCl + \downarrow Fe(OH)_3.$$

The oxides of the more negative elements combine with water to form acids; the oxides of the more positive elements unite with water to form bases. The acids and bases react to form salts, neutralizing each other with the elimination of water.

(Acid-forming oxide) $SO_3 + H_2O = H_2SO_4$ (sulphuric acid),
(Base-forming oxide) $Na_2O + H_2O = 2\ NaOH$ (sodium hydroxide),
(Neutral oxide) $4\ Fe + 3\ O_2 = 2\ Fe_2O_3$ (iron sesquioxide),
(Salt) $H_2SO_4 + 2\ NaOH = 2\ H_2O + Na_2SO_4$ (sodium sulphate).

Certain of the less positive and less negative elements form oxides, which act as acids toward strong bases and as bases toward strong acids: —

$SnO_2 + H_2O = SnO(OH)_2$ (metastannic acid),
$SnO(OH)_2 + 2\ H_2SO_4 = 3\ H_2O + Sn(SO_4)_2$ (stannic sulphate),
$H_2SnO_3 + 2\ NaOH = 2\ H_2O + Na_2SnO_3$ (sodium metastannate).

SULPHIDES

The binary compounds of sulphur, known as sulphides, resemble those of oxygen. The affinity of sulphur, however, for both positive and negative elements is less strong. Its compounds are less stable and the changes less numerous. All the sulphides, except those of the alkalies and alkaline earths, are insoluble in water. The sulphides of many positive elements are found in nature. In fact, this is the most general mode of occurrence of many of the elements. The most common ores of metals are the oxides and sulphides.

Formation of sulphides. 1. By the direct union of the elements with sulphur: —

$$Fe + S = FeS; \quad Cl_2 + S_2 = Cl_2S_2.$$

2. By the action of hydrogen sulphide, or soluble sulphides, upon a solution of the salts of positive elements: —

$$CuSO_4 + H_2S = \downarrow CuS + H_2SO_4,$$
$$FeSO_4 + (NH_4)_2S = \downarrow FeS + (NH_4)_2SO_4.$$

Some of the sulphides are soluble in hydrochloric acid: —

$$FeS + 2\,HCl = FeCl_2 + H_2S.$$

The sulphides vary in their solubility in different solvents, and many have different colors. These facts are taken advantage of in detecting many of the elements, especially those of metallic character (qualitative analysis). For instance, they may be classified in three groups: —

1. The sulphides soluble in water, hydrochloric acid, and ammonium hydroxide: alkaline sulphides, as Na_2S, K_2S_5; alkaline earth sulphides, as CaS, BaS.

2. Sulphides soluble in hydrochloric acid, but insoluble in water and ammonium hydroxide: FeS, CoS, NiS (all of which are black), ZnS (white), MnS (pinkish).

3. Sulphides insoluble in hydrochloric acid: PbS, Ag_2S, Hg_2S, CuS (all of which are black), HgS (black, lighter until an excess of reagent has been added; sometimes brilliant red), CdS, As_2S_3, SnS_2 (all yellow), Bi_2S_3, SnS (both brown), Sb_2S_3 (orange-red).

HYDROSULPHIDES

In striking analogy to the hydroxides we have the hydrosulphides, or sulphydrates, which may be looked upon as sulphides united to hydrogen sulphide: —

$$Na_2O + H_2O = 2\,NaOH, \quad CaO + H_2O = Ca(OH)_2;$$
$$Na_2S + H_2S = 2\,NaSH, \quad CaS + H_2S = Ca(SH)_2.$$

These compounds are doubtless formed when a solution of the alkaline and alkaline-earth sulphides is made in water.

As in the case of the oxides, the sulphides may be base-forming or acid-forming. The hydrosulphides of strong positive elements are bases; of these, only the hydrosulphides of alkalies and alkaline earths are known. The hydrosulphides of the negative elements are acids, thio-acids. Very few of them are known in the free state, though their salts are known, for example: As_2S_5, Sb_2S_3, SnS_2, and H_3AsS_4, H_3SbS_3, H_2SnS_3.

Selenium and *Tellurium* do not form as stable compounds as oxygen and sulphur. A few of their compounds with electro-positive elements, as gold and silver, are found in nature and constitute important ores of those metals.

EXERCISES

1. Write the equation, according to the first method, for producing (*a*) Fe_2O_3 from FeS_2; (*b*) Sb_2O_3 from Sb; (*c*) TeO_2 from $AuTe_2$.

2. Do the same according to the second method for (*a*) SrO from $SrCO_3$; (*b*) ZnO from $Zn(OH)_2$; (*c*) Al_2O_3 from $Al(OH)_3$.

3. Write the equation for preparing by the first method (*a*) P_2S_5 from P; (*b*) HgS from Hg.

4. Do the same by the second method for (*a*) Ag_2S from Ag_2NO_3; (*b*) Bi_2S_3 from $BiCl_3$; (*c*) ZnS from $ZnCl_2$; (*d*) MnS from $MnSO_4$.

CHAPTER XXXIV

OXIDES, HYDROXIDES, SULPHIDES, AND HYDROSULPHIDES OF GROUP I

POSITIVE SERIES

Li_2O	Na_2O	K_2O	Rb_2O	Cs_2O
——	Na_2O_2	——	Rb_2O_2	Cs_2O_2
——	——	K_2O_4	Rb_2O_4	Cs_2O_4
LiOH	NaOH	KOH	RbOH	CsOH
Li_2S	Na_2S	K_2S	——	——
LiSH	NaSH	KSH	——	——

The oxides and sulphides may be prepared by the first general method.

The oxides are deliquescent, soluble, caustic, alkaline substances. They combine with water, generating heat to produce the hydroxides: — $M_2O + H_2O = 2\ MOH$. The hydroxides are used in place of the lower oxides, because they are more easily prepared and handled. The hydroxides absorb water and combine with carbon dioxide.

Lithium Oxide, Li_2O. When heated, lithium burns in the air, giving a white oxide. The oxide is also produced by heating lithium nitrate. It is a white, crystalline mass, which slowly dissolves in water, forming LiOH. Lithium salts are too rare and expensive for common use. The most important salts are the carbonate and chloride.

Sodium Monoxide, Na_2O. Sodium forms two oxides, Na_2O_2 being the second. When the metal is heated in the air, the two are formed together. Also, $2\ NaOH + Na_2 \xrightarrow{} 2\ Na_2O + H_2$. It is a grayish white mass, melting at a red heat.

Sodium Hydroxide, sodium hydrate, caustic soda, $NaOH$, is prepared by two characteristic methods: —

1. $Na_2CO_3 + Ca(OH)_2 \xrightarrow{} \downarrow CaCO_3 + 2\ NaOH$.
2. By electrolysis,

$2\ NaCl + 2\ H_2O \xrightarrow{} 2\ NaOH + \uparrow H_2 + \uparrow Cl_2$ (Castner process). The hydrogen and chlorine are led away in separate pipes.

Sodium hydroxide is a white solid which combines readily with the moisture and carbon dioxide of the air. The caustic may be melted, but it is decomposed at a very high temperature. $NaOH$ forms a solid with water, $NaOH, 2\ H_2O$, at 0°, which melts at + 6°. Caustic soda is a corrosive poison, but has extensive use in the manufacture of soaps, in the decomposition of silicates in making water glass, and so forth.

Sodium Dioxide, Na_2O_2, is a slightly yellowish, deliquescent substance, which readily absorbs carbon dioxide. On the addition of water, the solid is decomposed with the production of much heat and the formation of the hydroxide and oxygen: — $Na_2O_2 + H_2O = 2\ NaOH + O$. On account of the production of oxygen it is extensively used in oxidizing and bleaching (oxone). When brought in contact with a combustible substance and a little water, rapid oxidation results, hence great care must be exercised in handling it.

There seems to be another oxide, with the formula Na_4O, but little is known about it.

Potassium Monoxide, K_2O. Potassium also forms two oxides, the other oxide being K_2O_4, which is a dark yellow substance, possessing powerful oxidizing properties. On the addition of water so much energy is liberated that it becomes red-hot. At the same time a peculiar odor is noted.

Potassium Hydroxide, potassium hydrate, caustic potash, KOH, is a deliquescent, very soluble substance which melts easily and may be volatilized. The water solution has a strong alkaline taste and peculiar odor. It resembles caustic soda in other properties. It is soluble in alcohol.

Rubidium and *Cæsium* form oxides and hydroxides analogous to those already mentioned. Little is known of them, however.

Rubidium Dioxide, RbO_2, is a dark brown, crystalline substance which dissolves in water with a hissing sound and the evolution of oxygen.

Ammonium Hydroxide, ammonia hydrate, spirits of hartshorn, NH_4OH, may be classed with this group, as it is strongly basic and resembles the alkalies. It is formed by the solution of ammonia in water. It has never been separated from the solution or prepared free from water. The solution gives off ammonia at ordinary temperatures. With acids it gives ammonium salts: —

$$NH_4OH + HCl \underline{\rightarrow} NH_4Cl + H_2O.$$

Sodium Sulphide, Na_2S. When hydrogen sulphide is led into a solution of $NaOH$, this reaction takes place: —

$$NaOH + H_2S \underline{\rightarrow} H_2O + NaSH.$$

On the addition of an equal amount of the hydroxide sodium sulphide is formed: —

$$NaSH + NaOH = H_2O + Na_2S.$$

Sodium sulphide is also formed by heating sodium sulphate and carbon together: —

$$Na_2SO_4 + 4\,C \underline{\rightarrow} \uparrow 4\,CO + Na_2S.$$

It is often formed, with higher sulphides, when a sulphur compound is fused with sodium carbonate on charcoal.

Sodium sulphide is a colorless or slightly colored solid, very soluble in water, giving a colorless solution at first. It acquires a yellow color from decomposition and formation of higher sulphides. It is used as a laboratory reagent, but is generally replaced by ammonium sulphide.

The higher sulphides are: — Na_2S, Na_2S_3, Na_2S_4, and Na_2S_5. They are formed by the solution of sulphur in any of the lower sulphides.

Sodium and *Potassium Hydrosulphides*, NaSH and KSH, are made according to the reaction given above; also, when H_2S is passed over the heated metals: —

$$2\,K + 2\,H_2S = H_2 + 2\,KSH.$$

Ammonium Sulphide, $(NH_4)_2S$, is formed by leading hydrogen sulphide into ammonium hydroxide until saturated and then adding an equal quantity of ammonium hydroxide. This is a colorless solution which dissolves sulphur, producing higher sulphides, the chief one being $(NH_4)_2S_5$. A water solution of the polysulphide is yellow. Ammonium sulphide is used extensively in the laboratory.

NEGATIVE SERIES

Cu_2O	Ag_2O	Au_2O
CuOH	AgOH	AuOH
CuO	Ag_2O_2	——
$Cu(OH)_2$	——	——
——	——	Au_2O_3
——	——	$Au(OH)_3$
Cu_2S	Ag_2S	——
CuS	——	——

Cuprous Oxide, Cu_2O, is found in nature as red copper ore (cuprite). It may be formed by heating copper in oxygen insufficient to form the higher oxide. It is usually prepared indirectly (see below). The red powder is stable when dry, but when moist it absorbs oxygen. It gives glass a red color.

Cupric Oxide, CuO, also occurs naturally, but not so abundantly. It is prepared by heating the nitrate, carbonate, hydroxide, or the metal, in the air or oxygen. It is a black solid, insoluble in water. It is stable even at higher temperatures, but loses its oxygen on being heated with reducing substances, such as hydrogen or carbon compounds. It colors glass green. It dissolves in acids, giving cupric salts: —

$$CuO + H_2SO_4 \rightleftarrows CuSO_4 + H_2O.$$

Cuprous Hydroxide, CuOH, is obtained as follows: —

$$CuCl + NaOH \rightleftarrows NaCl + CuOH.$$

It is a yellow powder, easily absorbing oxygen from the air, becoming blue and changing into the higher hydroxide, $Cu(OH)_2$. It is decomposed on heating with the formation of cuprous oxide.

Cupric Hydroxide, $Cu(OH)_2$, is prepared as follows: —

$$CuSO_4 + 2\,NaOH \rightleftarrows Cu(OH)_2 + Na_2SO_4.$$

It is a light turquoise-blue jelly, insoluble in water. On boiling the freshly precipitated hydroxide, it loses its water and is partially changed into the oxide: —

$$Cu(OH)_2 \rightleftarrows CuO + H_2O.$$

Substances containing hydrogen and oxygen as hydroxyls, as a rule, decompose on heating, with the elimination of water (see general methods). The degree of heat necessary to bring about this change is characteristic for each substance. Elements weak in chemical affinity do not hold the hydroxyl groups as firmly as the more active elements. The hydroxide of copper begins to decompose below + 100°. With some substances it is not necessary to remove the water from the sphere of the reaction. For example, if we boil CuOH suspended in water, the hydroxide is decomposed: —

$$2\,CuOH \rightleftarrows Cu_2O + H_2O.$$

Cupric hydroxide, when dry, is not so easily decomposed. If the fresh precipitate is dissolved in ammonium hydroxide, it forms a deep azure-blue solution. This solution will dissolve cellulose. Cupric hydroxide is not dissolved by sodium hydroxide unless certain organic substances, as tartrates, glycerol, and so forth, are present. If they are present, a deep blue liquid is obtained. If a reducing substance, like grape sugar, is added to the liquid, $Cu(OH)_2$ is reduced to CuOH, which separates. On boiling, the red Cu_2O is formed. These facts are utilized in determining the amounts of reducing substances in urine, for example, sugar.

Silver Oxide, Ag_2O. Silver does not combine with oxygen when heated in the air. It is prepared by precipitating a solution of silver nitrate by an alkaline hydroxide. We should expect $AgNO_3 + NaOH = AgOH + NaNO_3$, but this hydroxide does not exist at ordinary temperatures. The moist oxide acts in many ways like an hydroxide. It is even less stable than cuprous hydroxide, being decomposed into silver oxide and water at — 40°. It is an almost black powder, insoluble in water, and is alkaline in reaction. It absorbs carbon dioxide from the air. It is reduced by hydrogen at + 100° and decomposed by heating to a temperature of + 250°. Ozone oxidizes silver directly.

Argentous Oxide, silver suboxide, Ag_4O, is said to be formed by the reduction of silver salts. *Silver Dioxide*,

Ag_2O_2, is formed by the action of ozone upon silver. The important silver salts are formed after the type, Ag_2O.

Gold Monoxide, aurous oxide, Au_2O. Gold also forms auric oxide, Au_2O_3. These are both prepared indirectly. When cold dilute potassium hydroxide is added to aurous chloride, the former oxide is produced as a violet colored powder which is decomposed at +250°. It is readily decomposed by alkalies, but not much affected by the acids.

Gold Trioxide, auric oxide, Au_2O_3, a dark, insoluble powder, is obtained by heating the hydroxide to +100°. It is decomposed by further heating.

Gold Hydroxide, auric hydroxide, $Au(OH)_3$, is best prepared by heating gold trichloride with an excess of magnesia. If prepared by an alkaline hydroxide, some of the alkali is retained. It is a brown powder, decomposing in the light or on heating to +100°. It is a weak base, forming auric salts with strong acids. It readily loses one molecule of water, formic auric acid, AuO,OH, which reacts with strong bases to give aurates: —

$$AuO,OH + NaOH = H_2O + NaAuO_2.$$

By the action of ammonia upon moist silver oxide or upon gold hydroxide, peculiar compounds are obtained; these are respectively called "fulminating silver," Ag_2O, $2\,NH_3$, and "fulminating gold." Both are explosive.

The *sulphides* of copper and silver are closely analogous to the oxides. Several of them occur in nature, as copper glance, Cu_2S; blue copper, CuS; silver glance, Ag_2S. Chalcopyrite, Cu_2S, Fe_2S_3, is one of the most important ores of copper, as is also bornite, $3\,Cu_2S, Fe_2S_3$. There is some question as to the existence of gold sulphide.

EXERCISES

1. Why should the hydrogen and chlorine be led away in separate pipes in the Castner process ?

2. Write the equations for the preparation of colorless ammonium sulphide.

3. Write the reactions which take place when silver sulphide (Ag_2S) is roasted.

CHAPTER XXXV

OXIDES AND SULPHIDES OF GROUP II

THE type formulas for this group are, MO, MS, $M(OH)_2$, and $M(SH)_2$. The members of the positive series also form a dioxide according to the type MO_2. Two members of the negative series form oxides according to the type M_2O.

POSITIVE SERIES

BeO	MgO	CaO	SrO	BaO
$Be(OH)_2$	$Mg(OH)_2$	$Ca(OH)_2$	$Sr(OH)_2$	$Ba(OH)_2$
——	MgO_2	CaO_2	SrO_2	BaO_2
BeS	MgS	CaS	SrS	BaS
——	——	$Ca(SH)_2$	$Sr(SH)_2$	$Ba(SH)_2$

Both of the general methods are applicable for the preparation of the oxides and sulphides. The oxides of the positive series are basic and caustic, but are less caustic than the alkalies. The oxides of the positive group are not found in nature. An impure magnesium hydroxide is found, however.

Magnesium Oxide, magnesia, MgO, may be obtained by heating the carbonate, when it is called "magnesia usta." It is also prepared by the ignition of metallic magnesium in the air. It is a very light, white, tasteless powder which melts without decomposition. It slakes very slowly with water, forming —

Magnesium Hydroxide, $Mg(OH)_2$, which gives an alkaline reaction with litmus paper. It is usually prepared by treating a soluble salt with a soluble base:—

$$MgCl_2 + 2\,NaOH \rightarrow \downarrow Mg(OH)_2 + 2\,NaCl.$$

When this is suspended in water it is used medicinally as "milk of magnesia." It neutralizes acids. When ignited, it is converted into the oxide and is then used for the lining of crucibles and converters.

Calcium Oxide, quick-lime, CaO, is obtained by heating marble or limestone according to processes which may be continuous or intermittent. The rock shrinks about fifteen per cent., but loses about forty per cent. in weight.

$$CaCO_3 \rightleftarrows CaO + CO_2.$$

Lime is a white mass which fuses at + 2500°. When heated by an oxyhydrogen flame, which has a temperature of + 2100°, it produces a brilliant light known as the Drummond or lime light. Lime is a strongly caustic substance. It combines with water with the generation of much heat (slaking) to form —

Calcium Hydroxide, slaked lime, $Ca(OH)_2$: —

$$CaO + H_2O \rightleftarrows Ca(OH)_2.$$

Calcium hydroxide is mildly caustic. It is a white powder, slightly soluble in water, 1 : 760. The perfectly clear solution is known as "lime-water" and is used in medicine. It has a strongly alkaline reaction, and neutralizes acids. When calcium hydroxide is stirred up with water, it is called "milk of lime." Lime is a very important material, extensively used in commerce. It is always more or less impure. When the amount of impurities is small, it is known as "fat lime"; when the impurities are high in percentage, "poor lime."

Lime is used in making mortar. One part by weight of lime is slaked with from three to six parts of water. If this milk of lime is allowed to dry, it forms a film which on further drying cracks, owing to shrinkage. If this milk of lime is diluted, as it were, by the addition of sand (three to four parts), the shrinkage is largely overcome. The cream forms a coating over the grains of sand and on drying causes what is known as the setting of mortar. Gradually the calcium hydroxide absorbs carbon dioxide from the air, bringing about a hardening of the mortar, due to the formation of calcium carbonate: —

$$Ca(OH)_2 + CO_2 \rightleftarrows CaCO_3 + H_2O.$$

It is thought also that some of the sand after a long period of time combines with lime to form a silicate according to the following reaction: —

$$Ca(OH)_2 + SiO_2 = CaSiO_3 + H_2O.$$

When lime is left exposed to the air, the moisture of the air slakes it, and the carbon dioxide of the air is fixed by the hydroxide formed. The product is then known as "air-slaked lime" and is useless for making mortar.

Calcium Dioxide, CaO_2, is prepared by adding hydrogen dioxide to lime-water. It usually crystallizes with $8\,H_2O$. When heated or brought in contact with organic matter, it gives up oxygen. Calcium dioxide is used in dentistry.

The corresponding strontium compounds are similar to those of calcium.

Barium Oxide, baryta, BaO, is made by heating a salt of barium with a volatile acid radical. *Barium Hydroxide* $Ba(OH)_2$ is made by the following reaction: —

$$BaCO_3 + C + H_2O\ (\text{steam}) = 2\,CO + Ba(OH)_2.$$

Barium hydroxide is comparatively soluble in water, being less soluble in hot than in cold water, which is unusual.

Barium Dioxide, BaO_2, is prepared by heating BaO in a stream of dry oxygen or by heating the hydroxide in the air at + 400°. If the temperature is raised to + 700°, the oxygen is given off; if the temperature is lowered, the oxygen is taken up again. It is a grayish, porous body, more fusible than BaO. It combines with water to form a hydrate, $BaO_2, 8\ H_2O$. It is used mainly for the preparation of hydrogen dioxide.

The *Sulphides* of this series are formed by the action of carbon at high temperature on the corresponding sulphates:—

$$CaSO_4 + 4\ C = 4\ CO + CaS.$$

The sulphides have the property of glowing in the dark after exposure to sunshine or strong light. They are the chief constituents of "luminous paint." The pure sulphides do not possess this property. *Calcium Sulphide*, CaS, is slightly soluble in water. It is a waste product in the Le Blanc soda process. The sulphur is partly recovered from it now. *Barium Sulphide*, BaS, is more soluble.

When treated with hydrogen sulphide, the sulphides are changed into the *hydrosulphides:* $BaS + H_2S = Ba(SH)_2$, analogous to $BaOH + H_2O = Ba(OH)_2$.

NEGATIVE SERIES

——	Cd_2O	Hg_2O
——	CdOH	(HgOH)
ZnO	CdO	HgO
$Zn(OH)_2$	$Cd(OH)_2$	$Hg(OH)_2$
——	——	HgO_2
——	——	Hg_2S
ZnS	CdS	HgS

These oxides differ from the former by not slaking with water and in being less basic. The hydroxides are obtained by precipitation and are less stable.

Zinc Oxide, ZnO, occurs as zincite, or red zinc ore. The color is due to impurities, for the pure oxide is white.

It may be prepared by burning the metal (zinc white). For medicinal use the carbonate is heated. It is a heavy white powder, yellow when hot, insoluble in water. It is used in making white paint, which does not darken when in contact with hydrogen sulphide.

Zinc Hydroxide, $Zn(OH)_2$, is obtained as a white powder by precipitating and drying the precipitate obtained in the following reaction : —

$$ZnSO_4 + 2\ NaOH = Na_2SO_4 + Zn(OH)_2.$$

This precipitate is insoluble in water. It loses water on being heated and is converted into the oxide. It is soluble in acids and alkalies : —

$Zn(OH)_2 + 2\ HCl \rightleftarrows 2\ H_2O + ZnCl_2$;

$Zn(OH)_2 + 2\ NaOH \rightleftarrows 2\ H_2O + Na_2ZnO_2$ (sodium zincate).

Cadmium Oxide, CdO, is a brown powder, obtained by burning the metal in the air. The *Hydroxide*, $Cd(OH)_2$, is a white precipitate, similar to the zinc compound. It is decomposed at + 300°. It absorbs carbon dioxide from the air.

Cadmous Oxide, Cd_2O, and its corresponding *hydroxide*, CdOH, are also known.

Mercurous Oxide, Hg_2O, is obtained by the action of alkalies on mercurous compounds : —

$$2\ HgNO_3 + 2\ NaOH \rightleftarrows 2\ NaNO_3 + H_2O + \downarrow Hg_2O.$$

The black insoluble powder, under the influence of light or moderate heat, undergoes the following change : —

$$Hg_2O = Hg + HgO.$$

Mercuric Oxide, HgO, is the red oxide. In early times this was called "red precipitate," or "precipitate per se." It is prepared by heating mercury in the air for a long time just below its boiling point or by heating the nitrate.

It is a very heavy, red, insoluble solid, with an alkaline reaction. It is decomposed by heat: — $2\ HgO \rightleftarrows 2\ Hg + O_2$. It may also be prepared by precipitating a solution of a mercuric salt with an alkali, when it forms an orange-yellow powder: —

$$Hg\,(NO_3)_2 + 2\ NaOH \rightarrow 2\ NaNO_3 + H_2O + HgO.$$

The hydroxides of both of these oxides do not exist at ordinary temperatures. At − 42°, HgOH is known. Note the similarity here with copper and silver, regarding the stability of the hydroxides, and the analogy to the former, regarding the valence of the elements.

The *Sulphides of the Negative Series* are *Zinc Sulphide*, sphalerite, or blende, ZnS; *Cadmium Sulphide*, greenockite, CdS; and *Mercuric Sulphide*, cinnabar, HgS. These constitute the chief ores of these metals. Mercuric sulphide is made by subliming a mixture of the elements: — $Hg + S = HgS$ (red); or by precipitation with H_2S: — $HgCl_2 + H_2S \rightarrow 2\ HCl + HgS$ (black).

The precipitate is black, but is converted into the red form by sublimation. It is then known as vermilion and is used as a pigment.

Mercurous Sulphide, Hg_2S, has been prepared by the action of concentrated sulphuric acid upon mercury at ordinary temperatures for a long period of time.

EXERCISES

1. How much lime is theoretically obtainable from 9 tons of limestone which is 97 per cent pure?

2. How much barium dioxide is necessary to make 5 pounds of a 4 per cent solution of hydrogen dioxide?

3. How much of a tenth-normal hydrochloric acid solution is necessary to neutralize 3 grams of strontium hydroxide?

CHAPTER XXXVI

THE OXIDES AND SULPHIDES OF GROUP III

THE type oxide of this group has the formula M_2O_3. These oxides are widely distributed in nature, but not in large quantities. They are very stable and are less basic than the oxides of the preceding group. They constitute the basis of what are known as the "earth oxides."

Boron Trioxide, boron anhydride, B_2O_3, may be obtained by burning boron in the air, but it is more usually prepared by heating the hydroxide, $B(OH)_3$, which occurs in nature. It is a white hygroscopic solid which melts without decomposition. It volatilizes at a white heat and unites with water to form boric acid. Many metallic oxides dissolve in boron oxide, when it is fused, giving glasses with characteristic colors.

Boron Hydroxide, orthoboric acid, boric acid, boracic acid, $B(OH)_3$, is formed by decomposing borax ($Na_2B_4O_7$, 10 H_2O) with a mineral acid, when it is obtained as fine crystals. It is found dissolved in certain lakes of Tuscany, Nevada, and California. It is a weak acid, the salts of which are found in the same places. On passing steam through a solution in which it is present, it is volatilized. It acts similarly with the vapor of alcohol, which burns with a green flame when boron hydroxide is present. When fused with salts of a mineral acid, as calcium sulphate ($CaSO_4$), the mineral acid is replaced; whereas a salt of orthoboric acid in a water solution is decomposed by a mineral acid.

Metaboric Acid, BO(OH), is obtained by heating orthoboric acid to + 100°. It is a white powder which, on heating with the positive elements of the first two groups, forms salts, metaborates.

Tetraboric Acid, $B_4O_5(OH)_2$. When orthoboric acid is heated a long time at + 140°, this reaction takes place: —

$$4\,B(OH)_3 = 5\,H_2O + B_4O_5(OH)_2.$$

This acid forms stable compounds with many metals, giving borates, the most important one being —

Borax, di-sodium tetraborate, $Na_2B_4O_7$, 10 H_2O. It occasionally occurs in solution in springs and lakes, as in Nevada, California, and Central Asia. The crude form, in which it is marketed, is called "tincal." It is white, crystallizing in monoclinic prisms. It is very soluble in water; at + 30°, 1 : 14; at + 100°, 1 : $\frac{1}{2}$. Its water solution is feebly alkaline. Sometimes it crystallizes in octahedra at + 70°, with 5 H_2O. It loses its water on heating and swells up (intumesces). At + 850°, all the water is expelled, and there results a glassy mass, called borax glass ($Na_2B_4O_7$), which possesses the property of dissolving many metallic oxides, forming colored glasses. It is used in soldering metals, in enamel work, in ceramics, in silk manufacture, and as a cleansing agent.

Borax and boric acid are antiseptic and are often used as preservatives of food. The use of such preservatives, however, is objectionable.

Boracite, 2 $Mg_3B_8O_{15}$, $MgCl_2$ (Stassfurt), *Colemanite*, $Ca_2B_6O_{11}$, 5 H_2O (Mono Lake), and $HCa(BO_2)_3$, 2 H_2O, are minerals from which much boric acid is prepared.

Aluminum Oxide, alumina, Al_2O_3, occurs nearly pure in hexagonal crystals in a number of minerals and precious stones, as ruby, sapphire, corundum, emery, and so forth.

They have an average specific gravity of 3.9 and are next to the diamond in hardness. Alumina may be prepared by heating the hydroxide or by precipitation of an alkaline aluminate by means of carbon dioxide: —

$$2\,NaAlO_2 + CO_2 = \downarrow Al_2O_3 + Na_2CO_3.$$

Obtained in this way it is a white powder which may be crystallized by melting and allowing it to cool under pressure (alundum). In this manner synthetic gems are made. This form is insoluble in water, but is soluble in strong acids, provided it has not been previously heated too strongly. After intense ignition it is very hard and is used for polishing glass and metal. It is very stable and is not decomposed at the highest temperature so far obtained. It dissolves in fused cryolite. In this condition it may be decomposed by an electric current, the metal separating at the negative pole (process of Hall).

Aluminum Hydroxide, $Al(OH)_3$. Several hydroxides occur naturally: hydrargillite, $Al(OH)_3$, diaspore, $AlO(OH)$, and bauxite, $(AlFe)_2O(OH)_4$. The type is prepared as a gelatinous precipitate by this reaction: —

$$Al_2(SO_4)_3 + 6\,NH_4OH \rightleftarrows 3\,(NH_4)_2SO_4 + \downarrow 2\,Al(OH)_3.$$

Freshly precipitated, it is easily dissolved in acids, but on long standing in water it becomes less soluble. It is used for the purification of water, because it has the power of removing not only suspended matter but even dissolved material. The jelly enmeshes bacteria and as it settles removes them. It is also used for fixing colors (mordant) and for tanning. For this purpose usually a salt that is readily decomposed or hydrolysed, as the acetate, is used. When prepared in a cold solution, it separates as a gelatinous precipitate, which may be filtered and purified by washing with water. If the purified body is added to a solution of aluminum chloride, it dissolves. The form is called a *hydrosol.* If the solution is heated, the jelly separates out. It is then called a *hydrogel.*

In studying osmosis, we learned that many substances pass through a membrane. These substances, as a rule, may be had in a crystalline condition; therefore, for many years those substances which would pass through a membrane when in solution were called *crystalloids.* A solid, like the gelatinous aluminum hydroxide, does not pass through a membrane. If we place a solution of the aluminum hydroxide in aluminum chloride in water (hydrosol) in an osmotic cell and run water in for some time, it will be observed that the crystalloid aluminum chloride passes through the membrane, leaving a perfectly clear solution behind. If the latter is heated, a jelly separates. That is to say, the hydrosol does not pass through the membrane. It is devoid of crystalline form. Such a substance is spoken of as a *colloid.* This illustrates a general principle of very wide application, known as *dialysis.* Very recently, however, it has been learned that some colloids in certain solutions will pass through particular membranes, so the distinction no longer holds (Kahlenberg). Also it has been learned that some crystalloids in certain solutions may be separated from other crystalloids by dialysis, when special membranes are used, and certain colloids may be separated from other colloids in the same manner. These facts, not yet thoroughly explained, are of fundamental importance, for under normal conditions of health those substances which constitute food of necessity pass into the blood by dialysis and are thus distributed throughout the animal system. At the same time the blood acquires the waste products of the tissues, and in its course comes into contact with various secretory organs of the body, the kidneys, for example, which in turn by dialysis remove certain substances and discharge them from the body.

Aluminates. Toward strong bases aluminum hydroxide acts as an acid; for example,

$$Al(OH)_3 + NaOH = 2\,H_2O + NaAlO_2.$$

The resulting compounds are derivatives of meta-aluminic acid, $AlO(OH)$. Several salts of this are found in nature; for example, spinel, $Mg(AlO_2)_2$; chrysoberyl, $Be(AlO_2)_2$; and gahnite, $Zn(AlO_2)_2$. Sodium aluminate is produced in preparing alumina from bauxite and is used as a mordant.

The other oxides of this group are not important. Lanthanum forms La_2O_3 and La_2O_5. Thallium forms Tl_2O and Tl_2O_3.

SULPHIDES

The *Sulphides* of Group III are formed only in the dry way, as they are decomposed by water: —

$$Al_2S_3 + 6\,H_2O = 2\,Al(OH)_3 + 3\,H_2S.$$

We would expect a soluble sulphide to precipitate the sulphide according to this reaction: —

$$Al_2(SO_4)_3 + 3\,(NH_4)_2S = 3\,(NH_4)_2SO_4 + Al_2S_3.$$

But, as shown in the first reaction, the aluminum sulphide is decomposed; so we write what actually takes place, as follows: —

$$\begin{aligned}&Al_2(SO_4)_3 + 3\,(NH_4)_2S + 6\,H_2O\\&\qquad \rightleftarrows 2\,Al(OH)_3 + 3\,(NH_4)_2SO_4 + 3\,H_2S.\end{aligned}$$

EXERCISES

1. Write the reaction for making orthoboric acid from borax, using hydrochloric acid.

2. Make a diagram showing the relationship among the acids of boron.

3. Complete this reaction: —

$$La_2(SO_4)_3 + 3\ (NH_4)_2S + 6\ H_2O \rightarrow$$

CHAPTER XXXVII.

OXIDES AND SULPHIDES OF GROUP IV. CARBONATES OF GROUP I

THE type oxide is MO_2. *Carbon Dioxide* and *Monoxide* have been studied.

Acid and Basic Salts. When carbon dioxide is dissolved in water, we have formed the hypothetical *carbonic acid*, H_2CO_3. Either one or both of the hydrogen atoms may be replaced by an electro-positive element or radical. When all the acid-hydrogen is thus replaced, we have what is known as a *normal salt*, as Na_2CO_3. When only a portion of the hydrogen is replaced, we have what is known as an *acid salt*, $NaHCO_3$. If we take a base composed of an electro-positive element or radical, containing two or more hydroxyls, as, for example, $Bi(OH)_3$, we may replace all of the hydroxyls by electro-negative elements or radicals and obtain a normal salt, as $BiCl_3$. If only a portion of the hydroxyls is replaced, we have a *basic salt*, $Bi(OH)_2Cl$. The salts of carbonic acid are called *carbonates* and we may appropriately study them at this point.

CARBONATES OF GROUP I

The carbonates of the positive members of this series are usually white crystalline solids, soluble in water, having an alkaline reaction and remaining stable up to the temperature of melting. The normal carbonates have the formula M_2CO_3, and the acid carbonates, or dicarbonates, the formula $MHCO_3$.

Sodium Carbonate, soda, laundry soda, Na_2CO_3, occurs naturally as natrona, dissolved in certain lakes of Egypt, South America, and the United States. It is also obtained from sea-weeds, the burned ashes of which were called "kelp" or "varec." The demand for it was so great that other processes were devised. Its manufacture is one of the most important industries and is known as the Alkali Industry.

There are three general processes for the preparation of sodium carbonate. They are given in some detail, as they illustrate the practical economic application of important principles. All of them start from sodium chloride, the cheapest and most abundant source of sodium and chlorine.

1. The Le Blanc process (1794):—

$$2\,NaCl + H_2SO_4 \rightleftharpoons Na_2SO_4 + \uparrow 2\,HCl.$$

The hydrogen chloride was allowed to escape in the air, until complaints of the injury produced on vegetation brought about the enactment of laws in England (Alkali Act, 1863, *et seq.*) which required its absorption. Its saving later constituted a large part, if not all, of the profit by this method. The sodium sulphate is mixed with carbon (ground charcoal or coke) and heated in a "balling" furnace to produce the sulphide of sodium:—

$$Na_2SO_4 + 4\,C \rightleftharpoons Na_2S + \uparrow 4\,CO.$$

This in turn is treated with water and limestone:—

$$Na_2S + CaCO_3 \rightleftharpoons Na_2CO_3 + CaS.$$

Sodium carbonate is dissolved in water and purified by crystallization, separating as $Na_2CO_3, 10\,H_2O$, or what is commonly called "sal soda." The sulphur is now recovered from the sulphide, which for years was a waste product.

It will be observed here that both the sodium and chlorine are saved, but sulphuric acid and limestone are used up.

2. The Solvay, or ammonia-soda process (1863) depends upon the formation of ammonium hydrogen carbonate, when ammonia and carbon dioxide are brought together in water: —

$$NH_3 + H_2O + CO_2 \xrightarrow{} NH_4HCO_3.$$

This, in contact with sodium chloride, under pressure at a temperature not above +40°, gives the following reaction: —

$$NH_4HCO_3 + NaCl \xrightarrow{} NaHCO_3 + NH_4Cl.$$

The sodium hydrogen carbonate, called sodium bicarbonate or dicarbonate, is much less soluble than the chloride, hence may be separated by evaporation and cooling. The crystals are then gently heated: —

$$2\,NaHCO_3 \rightleftarrows Na_2CO_3 + H_2O + CO_2.$$

The ammonia is expensive and must be used over again; it is recovered by the following reaction: —

$$2\,NH_4Cl + CaO \xrightarrow{} 2\,NH_3 + CaCl_2 + H_2O.$$

In the process all the sodium is obtained, but the chlorine is lost.

3. The Castner process (1888) depends upon the formation of sodium hydroxide, by electrolysis, and its conversion into the carbonate, by treatment with carbon dioxide, which is had in abundance from the fermentation industries: —

$$NaCl = Na + Cl;$$
$$2\,Na + 2\,H_2O \xrightarrow{} 2\,NaOH + H_2;$$
$$2\,NaOH + CO_2 \xrightarrow{} Na_2CO_3 + H_2O.$$

As the carbonate may be made from the dicarbonate, so the reverse change may also take place: —

$$Na_2CO_3 + H_2O + CO_2 \xrightarrow{} 2\,NaHCO_3.$$

Everything is saved. The cost essentially depends upon the price of the electric current used. The chlorine is partly absorbed by slaked lime to make "bleaching powder" and partly burned in the hydrogen generated to make very pure hydrochloric acid.

$Na_2CO_3, 10H_2O$ crystallizes in monoclinic prisms which crumble on exposure to the air on account of efflorescence. The crystals melt at + 50°. Sodium carbonate may also be had with 7 or 2 molecules of water. It is soluble in water; 100 parts dissolve 7 at 0° and 52 at + 38°. It is less soluble at a higher temperature, due doubtless to the formation of the lower hydrates, which are not as soluble as the decahydrate. All of the water is lost on heating. Its solution has a strong alkaline reaction and taste. It is known as soda ash, sal-soda, and washing soda, and is used in enormous quantities for making glass, paper, soap, and so forth.

Sodium Dicarbonate, or sodium hydrogen carbonate, $NaHCO_3$, is less alkaline and less soluble in water. It is decomposed on heating according to the reaction given. It is called cooking soda, and has many uses on account of the large amount of carbon dioxide contained in it. It is one of the chief constituents of baking powder. It effervesces when mixed with certain substances on account of the evolution of carbon dioxide: —

$$NaHCO_3 + HCl \underline{\rightarrow} NaCl + H_2O + \uparrow CO_2;$$

$$6\,NaHCO_3 + Al_2(SO_4)_3 \underline{\rightarrow} \downarrow 2\,Al(OH)_3 + \uparrow 6\,CO_2 + 3\,Na_2SO_4.$$

The use of aluminum compounds in baking powder is objectionable.

Potassium Carbonate, K_2CO_3, is obtained by leaching the ashes of land plants. 1000 parts of wood give 3.5 to 28 parts of ashes, or from 0.45 to 4 parts of "potashes." It is also obtained by leaching the ashes of sugar beets, from molasses residues, and in the purification of sheep suint. The crude material is purified by recrystallization and is then called "pearl-ash." It is usually a granulated, deliquescent powder, melting at +890°. The impure form contains much water and is called "potash alkali." Recently potassium carbonate has been made from potassium chloride by a modified Solvay process, trimethylamine, $N(CH_3)_3$, being substituted for ammonia.

Lithium Carbonate, Li_2CO_3, is the only one of these carbonates that is not readily soluble in water.

Ammonium Carbonate, $(NH_4)_2CO_3$, is known as "smelling salts."

Salts of *Percarbonic Acid*, $H_2C_2O_6$, are obtained by electrolysis of the acid carbonates. *Potassium Percarbonate* is obtained by electrolyzing a solution of potassium carbonate cooled to − 15°, when a slightly blue colored powder, $K_2C_2O_6$, separates. When heated to from + 200° to + 300°, it is decomposed into the carbonate and oxygen. Oxygen is also given off by the aqueous solution at + 45°. It is a powerful oxidizing agent, similar to hydrogen dioxide, and many dyes are bleached by it.

CARBONATES OF THE NEGATIVE SERIES OF GROUP I

These differ very much from the alkaline carbonates in solubility, stability, and the mode of preparation.

The *Copper Carbonates* occur in nature as green malachite, $CuCO_3, Cu(OH)_2$, and blue azurite, $2\,CuCO_3, Cu(OH)_2$. These carbonates are formed by the action of carbon dioxide and water upon copper or by the precipitation of copper salts with an alkaline carbonate. Only the basic carbonates are known. They are insoluble in water and are readily decomposed by heat.

The normal *Carbonate of Silver* is formed by precipitation:—

$$2\,AgNO_3 + Na_2CO_3 \xrightarrow{} \downarrow Ag_2CO_3 + 2\,NaNO_3.$$

EXERCISES.

1. Tabulate the materials used, saved, and wasted in the three processes mentioned for the manufacture of sodium carbonate.

2. How much sodium hydrogen carbonate should two tons of sodium chloride yield? How much hydrogen chloride?

CHAPTER XXXVIII.

CARBONATES OF THE REMAINING GROUPS

Many of the carbonates of Group II (type MCO_3) occur naturally. Most of them may be prepared by precipitation with a soluble carbonate. When made thus, they are white powders, nearly insoluble in water. They are also prepared by the action of carbon dioxide upon the oxide or hydroxide. They are decomposed by acids and heat.

Magnesium Carbonate, $MgCO_3$, occurs naturally as magnesite, or combined in varying proportions with calcium carbonate as dolomite ($x\,MgCO_3$, $y\,CaCO_3$). On precipitating a solution of magnesium sulphate with sodium carbonate, a hydrated basic carbonate [$3\,MgCO_3$, $Mg(OH)_2$, $4\,H_2O$] is formed. It is called "magnesia alba" and is used medicinally. The composition varies with the temperature, concentration of solution, and other conditions of precipitation. Magnesium carbonate is a white powder insoluble in water. It dissolves in water charged with carbon dioxide, due to the formation of an acid carbonate, $Mg(HCO_3)_2$. On heating to + 300°, the carbonate decomposes: — $MgCO_3 = MgO + \uparrow CO_2$.

Calcium Carbonate, $CaCO_3$, occurs in nature in many forms and with many names: aragonite, which is the rhombic crystalline form, sp. gr. 3; calcite, or Iceland spar, hexagonal and rhombohedral, sp. gr. 2.7; and some calcites which are amorphous and others which are pseudo-crystalline. The granular form is marble. Limestone, coral, shells, chalk, and marl are forms of calcium carbonate with more or less impurities. When prepared as follows, $CaCl_2 + Na_2CO_3 = 2\,NaCl + \downarrow CaCO_3$, it is called "precipitated chalk," and is used medicinally and for polishing. On passing CO_2 through lime-water, a precipitate is formed at first: — $Ca(OH)_2 + CO_2 = \downarrow CaCO_3 + H_2O$. On continuing the passage of the gas, the precipitate dissolves, due to the formation of the acid carbonate: — $CaCO_3 + H_2O + CO_2 = Ca\,(HCO_3)_2$. 1000 parts of water at + 15° will dissolve 0.385 gram of this substance. Its solution gives what is known as temporary hardness to water, for, on heating, the carbon dioxide is given off and $CaCO_3$ is formed, separating as a fine powder. When waters charged with the acid carbonate are exposed to the air, the change takes place very slowly. The carbonate separates as compact crystals, forming stalactites and stalagmites. When heated to a red heat, limestone breaks up: — $CaCO_3 \rightleftarrows CaO + \uparrow CO_2$. This decomposition takes place only to a limited extent when the carbonate is heated in a sealed tube, for the pressure exerted by the gas in the tube becomes equal to that of the carbon dioxide which tends to escape from the carbonate.

Strontium Carbonate, strontianite, $SrCO_3$, is decomposed at + 1000°. *Barium Carbonate*, witherite, $BaCO_3$, is decomposed at + 1400° to + 1500°. Their properties are very similar to those of calcium carbonate. However, as the molecular weight increases, the bodies are more insoluble and more difficult to decompose on heating.

Of the negative series, *Zinc Carbonate*, $ZnCO_3$, is found in nature as calamine, which is an important zinc ore. Basic zinc carbonates are also known.

The elements of smaller atomic weights in Group III show little tendency to form carbonates. When we would expect aluminum carbonate to be formed, it is decomposed by the water present, forming the hydroxide as in the case of the sulphide: —

$$2\,AlCl_3 + 3\,Na_2CO_3 + 3\,H_2O = 2\,Al(OH)_3 + 6\,NaCl + \uparrow 3\,CO_2.$$

Lanthanum Oxide, La_2O_3, however, combines readily with carbon dioxide to form the carbonate. It is found in nature as lanthanite, $La_2(CO_3)_3$.

No definite carbonates of the positive series of Group IV are known. This statement applies also to the negative series, with the exception of lead. This carbonate occurs naturally as cerussite, $PbCO_3$. Carbonic acid, H_2CO_3, is very unstable, readily breaking up, CO_2 being given off. Many of the salts of this so-called acid possess this property, and are readily decomposed by water, with loss of more or less of their carbon dioxide. Basic carbonates result. This is particularly true of artificially prepared *lead carbonate*, $2\,PbCO_3, Pb(OH)_2$, which is called white lead.

The historic Dutch process for the manufacture of white lead depends upon exposing rolls or buckles of thin lead in earthenware pots. The rolls are supported on false, perforated bottoms, below which is vinegar, or dilute acetic acid. These are covered with boards, upon which are placed either manure or spent tan bark, and then another row of boards, and so on until the room is filled. They are left so for several weeks. The heat generated by the fermentation of the manure partially volatilizes the acetic acid, which forms a basic lead acetate. This in turn is acted upon by the carbon dioxide, resulting from the fermentation, and forms basic lead carbonate. The process takes place from the surface and gradually works into the metal. When the action is completed, the rolls are taken out and the carbonate is removed from the lead and then ground. The reactions expressing these changes are: —

$$3\,Pb(C_2H_3O_2)_2 + 3\,Na_2CO_3 = 3\,PbCO_3 + 6\,NaC_2H_3O_2,$$
$$3\,PbCO_3 + H_2O = Pb_3(CO_3)_2,(OH)_2 + CO_2.$$

White lead is the basis of most paints. It is blackened by hydrogen sulphide, due to the formation of PbS.

With regard to the carbonates of the remaining groups, it may be said that carbon dioxide appears to form no combinations, except with certain elements of the positive series, or some having high atomic weights.

Manganese Carbonate, $MnCO_3$, occurs in nature as rhodochroisite.

Ferrous Carbonate, $FeCO_3$, occurs in nature as siderite. The basic carbonates of iron are often seen as "iron stains." The ferrous dicarbonate is held in solution in chalybeate waters. As soon as the excess of carbon dioxide is removed, the iron is deposited as a slimy mud, consisting of basic ferrous carbonate, which absorbs oxygen, becoming reddish brown with the formation of ferric compounds.

Bismuth forms several basic carbonates; one, for example, has the formula $(BiO)_2CO_3$.

SULPHIDES OF CARBON

Several sulphides of carbon probably exist, but the important one is carbon disulphide, CS_2, which is formed by the direct union of the elements, sulphur vapor being led over heated carbon: — $C + 2\,S = CS_2 - 19{,}600$ cal. This is done now in an electric furnace (process of Taylor). When pure, it is a colorless, rather pleasant smelling liquid; sp. gr. 1.29. On standing, however, it becomes somewhat colored and usually has a very disagreeable odor. It evaporates very readily and absorbs heat. While it has a b.-p. of + 47°, it remains a liquid down to − 116°. It refracts light strongly. It is very insoluble in water, but mixes with alcohol and ether in all proportions. It is a good solvent for oils, fats, sulphur, phosphorus, and iodine. It burns with a blue flame: —

$$CS_2 + 3\,O_2 = CO_2 + 2\,SO_2.$$

Corresponding to H_2CO_3, we should expect H_2CS_3, *Thiocarbonic Acid*, which may be looked upon as a result of the union of H_2S and CS_2. It is very unstable, but forms a series of stable salts. The best known one of these is calcium thiocarbonate, $CaCS_3$.

Salts of *Ortho-Thiocarbonic Acid*, $C(SH)_4$, or H_4CS_4, are known.

COS, *Carbon Oxy-sulphide*, is also known.

EXERCISES

1. How do the principles of vapor tension apply to calcium carbonate when it is heated in a closed tube?

2. What is the percentage of (*a*) barium oxide in witherite; (*b*) strontium oxide in strontianite; (*c*) zinc oxide in calamine?

3. Complete the reaction

$$x\,Al_2(SO_4)_3 + y\,Na_2CO_3 + w\,H_2O =$$

4. How much white lead should be obtained theoretically from 65 kilograms of lead?

CHAPTER XXXIX

SILICON OXIDES, SILICATES, GLASS, EARTHENWARE

Silicon Dioxide, silica, SiO_2, is the only solid oxide of silicon occurring in nature. *Silicon Monoxide*, "monox," SiO, is prepared by heating the dioxide mixed with carbon in a vacuum electric furnace (Potter). The oxides of carbon formed are removed from the sphere of reaction by the reduced pressure. It is a yellow-buff powder in such a fine state of subdivision that it remains suspended in water through a long period of time.

The natural silicon dioxide is one of the extremely important constituents of the earth's surface. It occurs as rock-crystal (hexagonal system), quartz, flint, agate, tridymite, and, in variable sized grains, as sand. It forms several of the precious stones, as amethyst, bloodstone, chalcedony, moss agate, and smoky quartz. It is one of the mineral constituents of many rocks, as granite and syenite. It has a specific gravity of 2.7.

Silicon dioxide may be prepared by heating the hydroxides, which are obtained by precipitation. This form is an amorphous powder with a specific gravity of 2.2, and is so fine that it may be poured from one vessel into another in a stream like a liquid.

Silica melts transiently at + 1800°, when it may be spun into wool or made into various shapes. When heated higher, it becomes a clear liquid, which on cooling crystallizes and is transparent like glass. In fact, it is more transparent than glass to light of certain wave lengths.

The invisible rays as short as 250 $\mu\mu$ pass through quartz vessels. Fused quartz is very hard and brittle, but possesses a small coefficient of expansion. A quartz vessel heated red hot may be plunged into cold water without being broken. Glass with similar treatment is shattered.

Silicon dioxide is insoluble in water and in all acids, except hydrofluoric acid:—

$$SiO_2 + 4\,HF \rightleftarrows \uparrow SiF_4 + 2\,H_2O.$$

It forms a soluble compound, a silicate, with the alkaline oxides, especially when heated:—

$$SiO_2 + 2\,Na_2O = Na_4SiO_4.$$

Silicon Hydroxide, silicic acid, orthosilicic acid, $Si(OH)_4$, is prepared by precipitating an aqueous solution of the alkaline silicates by means of a mineral acid:—

$$K_4SiO_4 + 4\,HCl = 4\,KCl + \downarrow H_4SiO_4.$$

All of the silicic acid does not separate as a gelatinous precipitate (hydrogel), some remaining in solution in water (hydrosol). The former is an almost colorless, gelatinous mass, which can be dried to a white powder. It easily loses part of the water, forming $SiO(OH)_2$, or *metasilicic acid*, and on further heating, *silica* (SiO_2). The silicic acids are insoluble in acids, but are soluble in alkalies.

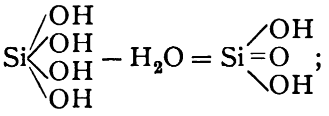
The salts of these acids are known as *silicates*. The soluble silicates, K_4SiO_4 or K_2SiO_3, and Na_4SiO_4 or Na_2SiO_3, are formed by fusing quartz or sand with the alkaline hydroxides. These are known as "water glass" and are soluble in water. They are used in surgical dressings, the manufacture of refractory cements, and in making glass.

Glass may be defined as an amorphous, transparent or translucent mixture of silicates, one of which is usually that of an alkali, with the general formula $M^{I}_2O, N^{II}O, 6 SiO_2$. M^{I} may be sodium or potassium, when the glass is known as a "soda" or "potash" glass; and N^{II} may be calcium or lead, when the material is known as a "lime" or "lead" glass. A "soda-lime" glass would have the generic formula $Na_2O, CaO, 6 SiO_2$. Glass is made by melting various substances, which, during the heating, yield the oxides referred to, in an open or covered pot constructed of clay, or in a special furnace. Often borates or phosphates are added to make the material melt at a lower temperature. Glass does not melt at a definite temperature, but, when heated, first softens and remains plastic through many degrees before becoming a limpid liquid. This conduct allows its working during the plastic stage by blowing, flattening, molding, and so forth. The constituents of which glass is made nearly always contain impurities, as the oxides of iron or other metals, which give the product color. In fact, many oxides or free metals are added to the "batch" to give glass a characteristic color. When colorless glass is wanted, the color effects produced by such impurities as iron are overcome by "bleaching." This is accomplished by adding manganese oxides in such proportions that the pink color produced by these oxides complements that resulting from the presence of the iron compounds and the glass appears colorless. Glass is known technically by other names than those which give an indication of its chemical composition; for instance, blown, window, crown, plate, cut, and so forth. These terms are associated with the devices used in producing a particular form, or the subsequent mechanical treatment to secure a particular finish. Glass is a mixture of silicates, some of which, if allowed to cool very slowly, solidify as crystals, and thus the glass is "devitrified." If glass is cooled too quickly, the exterior is hard but the glass is very brittle. It is aimed to cool the glass quick enough to avoid devitrification and at the same time to make it as tough as possible. As one of the silicates is that of an alkali, glass is always more or less soluble in water.

Other Silicates. A large portion of the earth's surface is made up of silicates, limestone being the chief additional formation. The silicic acids are quite unstable and are readily separated from their soluble salts by weak mineral acids. With these exceptions, the silicates are very stable. Many silicates are soluble in hydrochloric acid, and often during the solution one of the silicic acids separates out. All the silicates are acted upon more or less by hydrofluoric acid. Many are decomposed, however, only by fusion with the alkaline hydroxides or carbonates, which produce the silicates soluble in water or mineral acids.

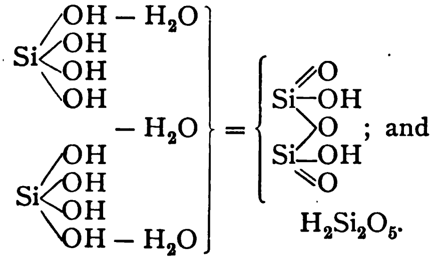
A study of the silicates is one of great interest and importance to the mineralogist, geologist, and agronomist. This brings to our notice the fourth desirable thing to know of compounds; namely, the relation of the atoms in the molecules. Confessedly, we do not actually know this relationship, nor are we able to depict it on a flat surface, but for the sake of convenience we make use of graphic formulas, which are most helpful in securing a better understanding of the constitution of many compounds, which otherwise appear quite complicated.

If we start with orthosilicic acid, one or more molecules, and remove water, molecule by molecule, we secure types like the following: —

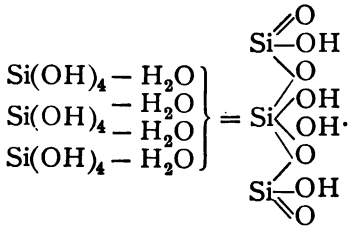


$$\mathrm{Si}\left\langle\begin{array}{l}\mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\\ \mathrm{OH}\end{array}\right. - H_2O = \mathrm{Si}\begin{array}{l}\diagup\mathrm{OH}\\ =\mathrm{O}\\ \diagdown\mathrm{OH}\end{array};$$

Orthosilicic acid. Metasilicic acid.

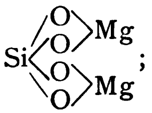


$H_2Si_2O_5$.

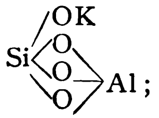


Trisilicic acid ($H_4Si_3O_8$).

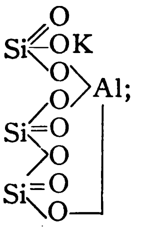
The last less H_2O gives $H_2Si_3O_7$; then $H_2Si_4O_9$, and so on, are obtainable. Several well known minerals are built up on these types.



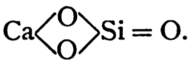
Mg_2SiO_4.
Olivine.



$KAlSiO_4$.
Mica.



$KAlSi_3O_8$.
Feldspar.



$CaSiO_3$.
Wollastonite.

Rocks are made up of mixtures; granite, for example, is composed of silica, mica, and feldspar. The soil is composed of mixtures of these silicates and others produced by their disintegration through chemical and physical influences. For example, feldspar is decomposed by long contact with water charged with carbon dioxide: —

$$2\ KAlSi_3O_8 + CO_2 + 2\ H_2O = 4\ SiO_2 + H_4Al_2Si_2O_9 + K_2CO_3.$$

The potassium carbonate is leached out by more water and thus becomes available as plant food. The hydrated aluminum silicate, $Al_2Si_2O_7$, $2\ H_2O$, which may be written Al_2O_3, $2\ SiO_2$, $2\ H_2O$, is known as kaolinite, or "primary," or "lean" clay, and has a granular structure somewhat similar to that of the original feldspar. When through mechanical influences it is pulverized, transported in suspension by water, and subsequently deposited, the particles become covered with a very thin coating of silicic acid, and the clay acquires new properties, such as plasticity. It is then known as kaolin, "secondary," or "fat" clay. The property of plasticity increases on standing in a damp condition, so clays are often "ripened" by keeping them wet for a number of months. Clay acquires a characteristic odor when breathed upon. When it is heated, water is lost, the material shrinks, and a hard, difficultly fusible porous mass remains. We are familiar with it in earthenware and bricks. To reduce the shrinkage to a minimum the clay is frequently mixed before shaping with pulverized feldspar and previously burned clay. The colors of earthenware are due to the impurities present, mainly compounds of iron. When the temperature is sufficiently high, the material fuses. Usually, however, clay is used as a basis for shaped vessels which are then baked; "biscuit firing" it is called. The rigid porous mass thus prepared is then dipped into a milk made of mixed fusible silicates suspended in water. On heating again, the silicates fuse and form an impervious coating or glass on the exterior; the resulting product is known as porcelain.

The term "clay," which means a substance of fairly definite composition to the chemist, is applied by the agronomist to rock of variable composition, but of such a state of subdivision that it is readily transported in suspension in water. Silt, which is composed of particles next greater in size mixed with clay, constitutes the basis of "alluvial soils."

EXERCISES

1. Calculate the percentage of silica in mica.

2. Suppose a glass had the formula Na_2O, CaO, $6\ SiO_2$, how much sodium carbonate and limestone would be necessary to make 250 pounds?

3. Write graphically the formula for dehydrated aluminum silicate.

CHAPTER XL

THE REMAINING OXIDES AND SULPHIDES OF GROUP IV

The Positive Series

TiO	——	CeO	——
$Ti(OH)_2$	——	$Ce(O)H_2$	——
Ti_2O_3	——	Ce_2O_3	——
TiO_2	ZrO_2	CeO_2	ThO_2
$Ti(OH)_4$	$Zr(OH)_4$	$Ce(OH)_4$	$Th(OH)_4$
$TiO(OH)_2$	$ZrO(OH)_2$	——	——
——	Zr_2O_5	——	Th_2O_5

Titanium Dioxide, TiO_2, may be prepared as a white powder, but it occurs in nature as rutile. It is widely distributed and is often found in iron ores. Its presence in iron ores has been regarded as very objectionable. However, with the modern methods of electric smelting of iron ores, it has proved to be less troublesome. The salts of metatitanic acid, H_2TiO_3, are important ores of titanium, as menaccanite, $FeTiO_3$, and perovskite, $CaTiO_3$. Polymetatitanic acid has the formula $H_{10}Ti_5O_{15}$.

Zirconium Dioxide, zirconia, ZrO_2, is found in nature as the precious stone hyacinth or jacinth. When prepared it is a white, difficultly fusible body which is used in the Linnemann and Nernst lights, and in incandescent gas mantles.

Thorium Dioxide, thoria, ThO_2, is the basis of the Welsbach incandescent gas mantle. *Cerium Oxide*, ceria, is usually present to the extent of one or two per cent. The mantle is made by saturating a fiber stocking with the mixed nitrates. After drying, the cotton is burned away. A network of the oxides remains behind, constituting the mantle, which is suspended above a Bunsen gas burner. The character of the light produced varies with the percentage of ceria present. The exact rôle played by the ceria has not been definitely explained. Its efficiency is probably due to the fact that the oxides of cerium are readily convertible one into the other. The gas mixture doubtless reduces and oxidizes the ceria, which changes facilitate the combustion of the gas by increasing the temperature.

The *Sulphides* of this series are made by fusion and are decomposed by water.

Negative Series

——	——	Pb_2O
GeO	SnO	PbO
$Ge(OH)_2$	$Sn(OH)_2$ $[Sn_2O(OH)_2]$	$Pb(OH)_2$
——	——	Pb_2O_3
——	——	Pb_3O_4
GeO_2	SnO_2	PbO_2
——	$SnO(OH)_2$ $(H_{10}Sn_5O_{15})$	$PbO(OH)_2$
GeS	SnS	PbS
GeS_2	SnS_2	——

Stannous Oxide, SnO, is made by heating stannous oxalate (SnC_2O_4) without the presence of air. It blackens on exposure to sunlight, absorbs oxygen, and is pyrophoric. The stannous salts, as $SnCl_2$, are derived from it.

Stannic Oxide, SnO_2, occurs in nature as tinstone or cassiterite, in quadratic crystals or in a compact brown mass with a specific gravity of 6.7. It is the sole source of tin. The artificial oxide is white, and is prepared by burning the metal in the air or by treating it with nitric acid and subsequently heating the product. Metastannic acid, $SnO(OH)_2$, and poly-metastannic acid, $H_{10}Sn_5O_{15}$, form soluble salts with the alkaline hydroxides. Na_2SnO_3, 3 H_2O is used as a "preparing salt" in calico printing.

The tin sulphides are formed by the precipitation of the corresponding salts with H_2S. *Stannic Sulphide*, SnS_2, is a yellow substance, which dissolves in alkaline sulphide solutions to form thio-salts: —

$$SnS_2 + Na_2S = Na_2SnS_3,$$

sodium thio-metastannate. When treated with an acid, the H_2SnS_3, which, one would expect, decomposes into SnS_2 and H_2S, the latter being evolved. *Stannous Sulphide*, SnS, is brown and insoluble in ammonium sulphide, $(NH_4)_2S$, but is soluble in the disulphide, $(NH_4)_2S_2$, the extra sulphur changing the tin from the stannous to stannic form (oxidation by sulphur): —

$$SnS + (NH_4)_2S_2 = (NH_4)_2SnS_3.$$

Lead Monoxide, litharge, massicot, PbO, is formed by heating lead in the air. It is a heavy, yellow-buff or reddish powder, stable when heated alone, but easily reduced by carbon or by hydrogen, and insoluble in water. It is used in the manufacture of red lead, glass, and the salts of lead, as the nitrate, acetate, and carbonate.

Red Lead, minium, Pb_3O_4, is prepared by carefully heating the monoxide in the air. It is a brilliant red, crystalline powder, with specific gravity of 8.6 to 9.1. It forms no hydroxide, is decomposed by acids, and appears to be composed of the monoxide and dioxide, 2 PbO, PbO_2, or Pb_2PbO_4.

Lead Dioxide, PbO_2, occurs naturally in small quantities as plattnerite. It is made artificially by treating red lead with nitric acid or chlorine. The brown powder is decomposed on heating into PbO and O, hence it has strong oxidizing power. The hydroxide, $PbO(OH)_2$, is known as metaplumbic acid.

The other lead oxides are thought to exist; namely, lead suboxide, Pb_2O, a black powder, easily decomposed by heat; and lead sesquioxide, Pb_2O_3, which may be considered a compound of the monoxide and the dioxide, PbO,PbO_2, or the lead salt of metaplumbic acid, $PbPbO_3$. It is a yellow powder which forms no class of compounds.

Lead Sulphide, PbS, occurs naturally as galena and is the chief ore of lead.

EXERCISES

1. If monazite sand contains 4 per cent of ThO_2, how many tons of the sand would be necessary to produce twenty-four million mantles, if each mantle weighed 6 grams?

2. How much red lead could be made from 800 kilograms of litharge?

3. Complete the reaction: —

$$x\ PbO_2 + y\ HCl = z\ PbCl_2 + w\ H_2O +$$

CHAPTER XLI

Group V

NITROGEN OXIDES AND THEIR DERIVATIVES

The oxides of nitrogen possess unique properties. They and their derivatives play such a prominent part in nature that their consideration involves some of the most important phenomena of both practical and theoretical interest. The comparable properties of the five oxides are set forth in the table. They present a splendid illustration of the law of multiple proportions.

Nitrogen	Monoxide, Nitrous Oxide “Laughing Gas”	Dioxide, Nitric Oxide	Trioxide	Tetroxide, Peroxide	Pentoxide
Formula	N_2O	N_2O_2 * (NO)	N_2O_3	N_2O_4 (NO_2)	N_2O_5
Physical state	gas	gas	gas	liquid	solid
Appearance	colorless	colorless	brown-red	colorless	white
Boiling point	− 89.8°	− 142°	− 3.5°	26°	+ 45°
Melting point	− 102.3°	− 150°	− 21°	− 11°	+ 30°
Specific gravity	1.53	1.039	1.45 (blue)	1.49 (red gas)	——
Spec. grav. liquid	0.937			1.50	
Corresponding acid	hyponitrous	none	nitrous	none	nitric
Formula	HNO		HNO_2		HNO_3
The sulphides are			N_2S_3	N_2S_4	N_2S_5

---

* NO is the actual formula. N_2O_2 is given to emphasize the law of multiple proportions.

Nitrogen Monoxide, nitrous oxide, "laughing gas," N_2O, is prepared by heating ammonium nitrate: —

$$NH_4NO_3 = \uparrow N_2O + 2\,H_2O.$$

It is a colorless gas with a pleasant smell and sweet taste, and is somewhat soluble in water and alcohol. It may be collected over warm water, in which it is only slightly soluble. It supports combustion, if the combustion has been actively started. A strongly burning taper is not extinguished by the gas; phosphorus burns brilliantly, whereas slowly burning sulphur does not burn in it. Davy learned that it could be breathed, and that it produced insensibility if inhaled long enough; therefore, it is used alone as an anesthetic in minor surgical operations, and followed by ether or chloroform in major operations. It does not combine directly with water to form an hydroxide.

Hyponitrous Acid, HNO, would appear to be the result of the following reaction: $N_2O + H_2O = 2\,HNO$. The compound is prepared indirectly, however. A hyponitrite is first produced by reducing a nitrite with sodium amalgam, and the hyponitrite is then decomposed by means of an acid. It is a very weak, unstable acid, and from its reactions cannot really be considered an hydroxide of nitrous oxide.

Nitrogen Dioxide, nitric oxide, N_2O_2, or NO, is prepared by the action of certain metals, as copper, upon nitric acid: —

$$3\,Cu + 8\,HNO_3 = \uparrow 2\,NO + 3\,Cu(NO_3)_2 + 4\,H_2O.$$

On coming in contact with oxygen or the air, brown-red fumes of the higher oxides are formed at once. It supports combustion, but less readily than nitrous oxide. Burning sulphur will be extinguished in it, but phosphorus will continue to burn. Mixed with carbon disulphide it burns with a brilliant light with high actinic properties. It is dissociated at elevated temperatures. It is neutral in reaction and forms no hydroxide or acid with water, in which it is insoluble. It is readily soluble in a solution of ferrous sulphate, which it colors brown. It is poisonous when breathed.

Nitrogen Trioxide, N_2O_3, is formed by the action of starch, sugar, arsenious oxide, or other easily oxidizable substances, upon nitric acid: —

$$As_2O_3 + 2\,HNO_3 + 2\,H_2O = \uparrow N_2O_3 + 2\,H_3AsO_4.$$

The blue liquid at low temperatures changes to a brown-red gas when heated. At ordinary temperatures it appears to be a mixture of NO and NO_2. It dissolves in ice-cold water, producing a blue liquid, which is *Nitrous Acid*, HNO_2: —

$$N_2O_3 + H_2O = 2\,HNO_2.$$

It is a very unstable acid and is known only in solution. It is easily decomposed into nitric acid and nitric oxide. The salts, *nitrites*, are fairly stable. They may be produced by the reduction of nitrates, sometimes by simply heating, or by the oxidation of ammonia. The nitrites occur naturally in the atmosphere, in rain and soil waters, and in plant and animal juices, but in very small amounts. When thrown upon hot charcoal, they deflagrate. Sodium nitrite is extensively used in making organic compounds. The nitrites are decomposed by stronger acids: —

$$2\,KNO_2 + H_2SO_4 = K_2SO_4 + 2\,HNO_2,$$

and $$3\,HNO_2 = HNO_3 + N_2O_2 + H_2O.$$

Nitrogen Tetroxide, nitrogen peroxide, N_2O_4, or NO_2, is formed when nitric oxide is brought in contact with the proper amount of oxygen: —

$$N_2O_2 + O_2 = N_2O_4.$$

It is also formed by the decomposition of some of the nitrates by heat: —

$$Pb(NO_3)_2 = N_2O_4 + PbO + O.$$

N_2O_4 is a colorless liquid at low temperatures, solidifying at $-20°$ C. On slight rise of temperature it is dissociated wholly into NO_2, which is a red-brown gas at $+140°$. It forms no distinctive hydroxide of its own, but on solution in water, nitrous and nitric acids are formed: —

$$2\,NO_2 + H_2O = HNO_2 + HNO_3.$$

It is a powerful oxidizing agent, but does not readily support combustion, although phosphorus can be made to burn in it. It is very poisonous when breathed.

Nitrogen trioxide and nitrogen tetroxide readily lose oxygen, changing into the dioxide, when brought in contact with a reducing substance, as sulphur dioxide. This is observed by the gases becoming colorless. When more oxygen is brought in contact with the nitrogen dioxide, the other oxides are re-formed and again exercise their oxidizing action. This property of causing free oxygen to combine with substances not so affected under normal conditions is taken advantage of in the manufacture of the most important of all chemicals, sulphuric acid.

Nitrogen Pentoxide, N_2O_5, is prepared by removing water from nitric acid by means of a powerful desiccating agent, as phosphorus pentoxide: —

$$2\,HNO_3 = H_2O + N_2O_5.$$

It is also prepared by the action of chlorine upon silver nitrate: —

$$2\,AgNO_3 + Cl_2 = 2\,AgCl + N_2O_5 + O.$$

Nitrogen pentoxide decomposes spontaneously. It combines with water with great energy to form nitric acid, which will be considered in the next chapter: —

$$N_2O_5 + H_2O = 2\,HNO_3.$$

EXERCISES

1. How much air would be necessary to change 6 liters of nitrogen dioxide into the trioxide? (Consider all measurements at 0° and 760 mm.)

2. How much nitrogen tetroxide may be made according to theory from 8 g. of lead nitrate?

3. What volume of "laughing gas," measured at + 20° and 750 mm., may be made from 12 g. of ammonium nitrate?

CHAPTER XLII

NITRIC ACID AND THE NITRATES

Nitric Acid, "aqua fortis," HNO_3, was one of the earliest known acids. It is formed in the process of decay of nitrogenous organic matter in the presence of an excess of oxygen and strong bases, by which it is at once neutralized. In this way we can account for the large deposits of nitrates found in various parts of the world, as the potassium nitrate (Bengal saltpeter) of India and Persia, and the sodium nitrate (Chili saltpeter) of Chili and Peru. It can be formed by the action of an electric spark upon moist air. It is therefore found in the air as a nitrate after electric storms and in rain water. Several modern methods for preparing this important acid depend upon duplicating natural processes in efforts to utilize the abundance of nitrogen in the atmosphere. For example, the air is sparked by high-tension currents, and the products resulting are quickly removed to a colder place, as they are readily decomposed at the elevated temperature. Nitric acid is usually prepared, however, by treating a nitrate with a stronger non-volatile acid, as sulphuric acid: —

$$2\,NaNO_3 + H_2SO_4 \rightleftarrows Na_2SO_4 + 2\,HNO_3.$$

The heating must be gentle, as the acid is decomposed at high temperatures. It is concentrated and purified by redistillation with sulphuric acid and passing air through it in the dark, since it is decomposed by bright light.

Nitric acid is ordinarily a colorless liquid, b.-p. + 86°, which becomes a solid at – 47°. The specific gravity of 99.8 per cent acid is 1.56. It fumes in the air and turns yellow in the light and on heating. This is due to partial decomposition, the oxides of nitrogen separating and dissolving in the acid. The effect of heat is to decompose it, as follows: $2\,HNO_3 = 2\,NO_2 + H_2O + O$. The ordinary concentrated acid contains 68 per cent acid, and has a sp. gr. of 1.42 and distills at + 123°. When the concentrated acid has dissolved nitrogen tetroxide until it has a specific gravity of about 1.5, it acquires a deep red color and is known as *fuming nitric acid.*

Nitric acid is extensively used in the separation of gold and silver, and in the manufacture of explosives, coal tar dyes, and synthetic medicinal preparations. It is a powerful corrosive poison. It colors the skin yellow and attacks organic matter vigorously. It is a strong oxidizing agent.

Action of Nitric Acid. — Usually when a metal is dissolved in an acid, hydrogen is evolved; with nitric acid, however, if any hydrogen is liberated, it reacts with more nitric acid. The reaction may be looked upon as taking place in two stages. If a strong acid is used, the reactions may be written so: —

$$3\,Zn + 6\,HNO_3 \rightleftharpoons 3\,Zn(NO_3)_2 + \uparrow 3\,H_2,$$

and $$3\,H_2 + 2\,HNO_3 = 4\,H_2O + \uparrow 2\,NO,$$

or $$3\,Zn + 8\,HNO_3 \rightleftharpoons 3\,Zn(NO_3)_2 + 4\,H_2O + \uparrow 2\,NO.$$

If we use a very weak acid (5–6 per cent), the reaction takes place in this way: —

$$Zn + 2\,HNO_3 \rightleftharpoons Zn(NO_3)_2 + \uparrow H_2,$$
$$2\,HNO_3 + 4\,H_2 = NH_4NO_3 + 3\,H_2O.$$

With some oxides the reaction is as follows: —

$$ZnO + 2\,HNO_3 \rightleftharpoons Zn(NO_3)_2 + H_2O.$$

With some elements, as, for example, tin and antimony, the acid exerts a powerful oxidizing action. The nitrates are not formed, nor are the metals brought in solution, but the oxides or hydroxides are produced. These are not soluble in nitric acid. White insoluble compounds are produced.

Aqua Regia is the name given to a mixture of concentrated hydrochloric and nitric acids, usually in the proportion of 3 : 1. Gold and platinum do not dissolve under ordinary conditions in either of these acids singly, but they dissolve readily in aqua regia. Its powerful solvent action is attributed to the formation of chlorine and nitrosyl chloride: —

$$3\,HCl + HNO_3 = 2\,H_2O + NOCl + Cl_2.$$

The Nitrates

Nitric acid is a monobasic acid and its compounds are called *nitrates*. Here we have hydrogen joined to an electro-negative radical. The nitrates are numerous and very important. They are usually crystalline solids, soluble in water, losing oxygen on being heated, and decomposing energetically when heated with oxidizable matter. They melt easily, and when heated on charcoal they deflagrate. Some nitrates of the less positive elements, as bismuth, are decomposed by water, forming basic nitrates similar to the basic chlorides.

Sodium Nitrate, cubic niter, Chili saltpeter, $NaNO_3$, is had in an impure form from Peru, Bolivia, and Dakota, called "caliche." Large quantities are used annually in the manufacture of sulphuric acid, also in the manufacture of inferior gunpowder, and in fertilizers. The commercial form usually carries about 98 per cent $NaNO_3$. It attracts moisture.

Potassium Nitrate, niter, saltpeter, Bengal saltpeter, KNO_3, is found in India, Persia, Egypt, and in the filthy parts of certain cities. It is formed by the decay of nitrogenous matter in rainless seasons and in sheltered places, when an alkaline base is present. These conditions are artificially produced in what are known as "niter-plantations." Nitrogenous organic matter, porous earth, wood ashes, and so forth, are heaped up and allowed to stand for many months. The mass is then leached and the solution evaporated until the niter crystallizes on cooling the concentrated liquor. The changes are the result of the action of the *Bacillus nitrificans*. Potassium nitrate is now largely made also by double decomposition:—

$$KCl + NaNO_3 = KNO_3 + NaCl.$$

This action is dependent upon the difference in solubility at different temperatures of the salts present. Potassium nitrate is not hygroscopic. It is used in the manufacture of the finer grades of gunpowder and other explosives, for making matches and fireworks, and for curing meat.

Gunpowder.—The knowledge of the propelling force of gunpowder-like mixtures came about between 1313 and 1325 A.D., and Berthold Schwarz, a Benedictine monk, invented the guns for utilizing this force (Guttmann). Gunpowder consists of an intimate mixture of saltpeter, 75 per cent, charcoal, 12 to 15 per cent, and sulphur, 13 to 10 per cent; its composition varies according to the purpose for which it is to be used. The finely pulverized materials are thoroughly ground together in a moist condition and then pressed into sheets, which are broken and dried. The moist mass may be pressed into molds of various sizes and shapes before drying. The force exerted in the explosion is due to the sudden production of a large amount of gas, which is greatly expanded by the high temperature generated in the combustion. The principal gases are carbon dioxide, carbon monoxide, nitrogen, and water; and the chief solid products are potassium carbonate, sulphide and sulphate, and free sulphur.

Silver Nitrate, lapis infernalis, lunar caustic, $AgNO_3$, is the chief salt of silver. It is made by solution of the metal in nitric acid, and subsequent evaporation to crystallization: —

$$3\,Ag + 4\,HNO_3 \rightleftharpoons 3\,AgNO_3 + 2\,H_2O + \uparrow NO.$$

It fuses at + 225° and may be cast in small sticks. It cauterizes organic matter and is poisonous. It is easily decomposed by contact with organic matter, as dust, paper, and the skin. It is the foundation of some indelible inks.

Calcium Nitrate, $Ca(NO_3)_2$, is sometimes found in nature in small amounts, as a result of similar changes noted in the formation of the alkaline nitrates. The anhydrous salt is used in the laboratory for drying nitrogen peroxide.

Strontium and *Barium Nitrates*, $Sr(NO_3)_2$ and $Ba(NO_3)_2$, are used in fireworks to produce red and green fires, respectively.

Lead Nitrate, $Pb(NO_3)_2$, is used in dyeing and calico printing, in the making of chrome-yellow, and in photography.

Ferric Nitrate, $Fe(NO_3)_3$, is used in dyeing silk black and cotton buff.

Basic Nitrates are formed by mercury, bismuth, iron, and some other metals.

Bismuth Subnitrate, bismuth oxynitrate, bismuthyl nitrate, $BiONO_3$, is used as a cosmetic, and in medicine.

EXERCISES

1. Write the reactions of hydrochloric and nitric acids upon zinc, one beneath the other, and compare the formulas.

2. Sodium and potassium chlorides and nitrates are soluble in water. Why then should potassium nitrate instead of sodium nitrate be obtained when a mixture of the salts in a water solution is evaporated ?

3. What is the percentage of nitrogen in "caliche" that is 97.8 per cent pure?

4. How much sodium nitrate (98 per cent pure) would have to be present in a fertilizer that contained 4 per cent of nitrogen, assuming that all the nitrogen came from the nitrate?

CHAPTER XLIII

OXIDES AND SULPHIDES OF THE OTHER ELEMENTS OF GROUP V

A TABLE showing the composition of the oxides and sulphides brings out the striking resemblances of the elements in this group: —

P_4O	P_2O	——	P_2O_3	P_2O_4	P_2O_5
——	——	——	As_2O_3	——	As_2O_5
——	——	——	Sb_2O_3	Sb_2O_4	Sb_2O_5
——	——	BiO	Bi_2O_3	Bi_2O_4	Bi_2O_5
P_4S	P_2S	——	P_2S_3	——	P_2S_5
——	——	As_2S_2	As_2S_3	——	As_2S_5
——	——	——	Sb_2S_3	——	Sb_2S_5
——	——	BiS	Bi_2S_3	——	——

Phosphorus Trioxide, P_2O_3, or P_4O_6, is formed by the slow oxidation of phosphorus at low temperatures or in a limited amount of oxygen. In contact with oxygen, it is oxidized to P_2O_5. The colorless needles, which melt at + 24°, have a garlic-like odor. They combine with water to form *phosphorous acid:* —

$$P_2O_3 + 3\,H_2O = 2\,H_3PO_3.$$

This acid is also produced by the decomposition of phosphorus trihalide by means of water: —

$$PCl_3 + 3\,H_2O = 3\,HCl + P(OH)_3.$$

It is a solid (m.-p. + 70°) which deliquesces to a thick sirup, absorbs oxygen from the air, and is reducing in its action. When heated, the following reaction takes place: —

$$4\,H_3PO_3 = PH_3 + 3\,H_3PO_4.$$

Although it has three hydrogen atoms, it is a dibasic acid. Its salts are called *phosphites*.

Phosphorus Pentoxide, P_2O_5, is formed when phosphorus is burned at a high temperature or in the presence of an excess of oxygen. It is a crystalline powder which volatilizes at + 250° and dissociates at high temperatures. It combines with water with a hissing sound and the production of much heat. Its strong attraction for water makes it a most valuable desiccating agent. It is used especially for drying gases.

In combining with water three reactions may take place, depending upon the proportions present: —

(*a*) $P_2O_5 + H_2O = 2\,HPO_3$ (metaphosphoric acid);

(*b*) $P_2O_5 + 2\,H_2O = H_4P_2O_7$ (pyrophosphoric acid);

(*c*) $P_2O_5 + 3\,H_2O = 2\,H_3PO_4$ (orthophosphoric acid).

Orthophosphoric Acid, H_3PO_4, is a crystalline solid, very soluble in water. The other phosphoric acids are usually made from it. When heated to + 400°, it loses a molecule of water and changes to metaphosphoric acid, which is called, commercially, glacial phosphoric acid. This acid coagulates albumen, whereas the others do not. When the temperature is maintained at + 200° to + 300°, one molecule of water is lost from two of orthophosphoric acid, and pyrophosphoric acid, $H_4P_2O_7$, is obtained. Metaphosphoric acid is monobasic, giving metaphosphates; pyrophosphoric acid is tetrabasic, giving pyrophosphates; and orthophosphoric acid is tribasic, giving orthophosphates. With the last we have three classes of salts, depending upon the replacement of one, two, or three hydrogen atoms, thus:—

Na_3PO_4, trisodium phosphate, or normal sodium phosphate;

Na_2HPO_4, disodium hydrogen phosphate; and

NaH_2PO_4, sodium dihydrogen phosphate.

The former of the two acid salts, like Na_2HPO_4, and $Ca_2H_2(PO_4)_2$, or $CaHPO_4$, are neutral in reaction, whereas the other acid phosphates, like NaH_2PO_4 and $CaH_4(PO_4)_2$, are acid in reaction.

We may substitute the hydrogen by different bases or radicals and obtain double phosphates, as NH_4MgPO_4 and NH_4NaHPO_4, H_2O. The latter is commonly called microcosmic salt, or salt of phosphorus.

Many of these phosphates occur widely distributed in nature, but usually in very small amounts. The alkaline phosphates are soluble in water, as are some of the acid phosphates, especially the dihydrogen phosphates. The monobasic hydrogen phosphates are less soluble, some being insoluble. The normal phosphates, as, for example, calcium phosphate, are insoluble. The phosphates are essential to plant and animal life. They occur in the soil, urine, and bones.

Calcium Phosphate, tricalcic orthophosphate, $Ca_3(PO_4)_2$, is the chief constituent in bones. They nearly always contain a small amount of magnesium phosphate as well. Calcium phosphate is found as phosphorite, apatite, and in phosphate rock; these are called mineral phosphates. They constitute the material from which phosphorus and its compounds are prepared. On treatment with an acid, like sulphuric acid, two phosphates are formed which are present in phosphatic fertilizers:—

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 = 2\ CaSO_4 + CaH_4(PO_4)_2,$$

or $$Ca_3(PO_4)_2 + H_2SO_4 = CaSO_4 + 2\ CaHPO_4.$$

The former is soluble in water and is easily assimilated by plants; while the latter is insoluble in water, and is known as "reverted" or "precipitated" phosphate. It is readily dissolved by dilute acids and certain salts of ammonium, as ammonium citrate. It is supposed to be soluble, therefore, in plant juices and taken up as food by the plants. The normal tricalcium phosphate is dissolved only by strong acids.

Iron and *Aluminum Phosphates* occur naturally and are insoluble in water.

Hypophosphorous Acid, H_3PO_2, is obtained by the decomposition of the phosphides of Group II with water, or as follows: —

$$4\,P + 3\,NaOH + 3\,H_2O = 3\,NaH_2PO_2 + \uparrow PH_3.$$

Below zero it is obtained as white leaflets, which melt at + 17.4° but decompose on heating. It does not alter in the air when dry, but when moist easily absorbs oxygen. Hypophosphorous acid is monobasic, only one of the hydrogen atoms being replaced by an electro-positive element or radical. It is used in medicine and constitutes the basis of Horsford's phosphates.

Phosphorus Sulphides, P_4S, P_2S, P_2S_3, P_2S_5, are used in organic chemistry for the production of thio-compounds.

ARSENIC COMPOUNDS

Arsenic Trioxide, As_2O_3, occurs in nature in small quantities and is known as "bloom." However, it is usually prepared by roasting arsenic ore in the air. The white powder obtained is known as "white arsenic" or "poisonous flour." This, when melted, forms "arsenic glass." It is hard and vitreous with a sp. gr. of 3.69. It gradually changes to "arsenic porcelain," becoming opaque and white, with a sp. gr. of 3.78. It has no odor, but a slightly sweetish taste. It melts at + 200°, crystallizing in octahedra on cooling. It sublimes at + 218°. When the vapors are quickly cooled, they crystallize in rhombic prisms. It is slightly soluble in water and this solution acts as if it contained arsenious acid (H_3AsO_3), being weakly acid to litmus. The oxide dissolves in hydrochloric acid. It is an irritant poison. As an insecticide it is used in mounting skins. Arsenic trioxide is also used in "fining" glass.

Arsenites.—The existence of arsenious acid (H_3AsO_3) is hypothetical, but a number of arsenites are known. They are very powerful reducing agents and are poisonous. The alkaline arsenites are soluble in water. They crystallize poorly and are deliquescent. Copper arsenite is a brilliant green salt, Scheele's green, which is used as a pigment and as an insecticide. Paris green, Schweinfurt or emerald green, is the double arsenite and acetate of copper [$Cu_3(AsO_3)_2$, $Cu(C_2H_3O_2)_2$.]

Arsenic Pentoxide, As_2O_5, does not occur in nature, but is prepared by oxidizing the trioxide with nitric acid. $AsO(OH)_3$ is produced, which loses water on heating, leaving As_2O_5. It is a white deliquescent mass, melting when heated. On elevation of temperature, it decomposes into arsenic trioxide and oxygen.

Arsenic Acids.—We have an orthoarsenic acid corresponding to orthophosphoric acid:—

$$As_2O_5 + 3\,H_2O = 2\,H_3AsO_4,$$

which combines with ½ water to form a solid which melts at + 100°. This heated carefully to + 140–150° gives pyroarsenic acid ($H_4As_2O_7$). When heated to + 200°, metarsenic acid is obtained ($HAsO_3$). Orthoarsenic acid is a crystalline solid with a very unpleasant taste, and is poisonous. It is a caustic. These acids combine with bases and form a series of arsenates similar to the phosphates.

Arsenic Sulphides.—Arsenic forms three sulphides. The trisulphide (As_2S_3), which occurs in nature as orpiment or auri-pigment, is yellow. As_2S_5, arsenic pentasulphide, is had by precipitation of solutions of arsenates with sulphuretted hydrogen; this precipitate is also yellow. Another sulphide, As_2S_2, the disulphide, occurs in nature and is called realgar. It is ruby-red (sp. gr. 3.5). The sulphides of arsenic are soluble in ammonium sulphide and form thio-arsenites and arsenates. Solutions of Na_3AsS_3 and Na_3AsS_4, when heated with acids, decompose with the evolution of hydrogen sulphide and the precipitation of the sulphides:—

$$2\,Na_3AsS_4 + 6\,HCl = 6\,NaCl + 3\,H_2S + As_2S_5.$$

ANTIMONY COMPOUNDS

Antimony Trioxide, Sb_2O_3, occurs free in nature. It is formed by burning antimony in the air. It is a white powder insoluble in water. When heated in the air, it changes into the tetroxide. It dissolves in a water solution of an alkaline hydroxide, giving salts called metantimonites:—

$$Sb_2O_3 + 2\,KOH = H_2O + 2\,KSbO_2.$$

Antimony trioxide forms two hydroxides, $Sb(OH)_3$, or orthoantimonious acid, and $Sb_2O(OH)_4$, pyroantimonious acid. With strong acids, it acts as a base, and there is a great tendency to form basic salts. When a carbonate is added to a chloride, the following reaction takes place:—

$$2\,SbCl_3 + 3\,Na_2CO_3 + H_2O = 2\,SbO,OH + 6\,NaCl + 3\,CO_2.$$

Antimony Pentoxide, Sb_2O_5, is prepared by oxidizing the element or trioxide. It is yellow and very insoluble in acids; it loses oxygen when heated. Three hydroxides can be prepared from it: orthoantimonic acid, H_3SbO_4, pyroantimonic acid, $H_4Sb_2O_7$, and metantimonic acid, $HSbO_3$.

Antimony Tetroxide, Sb_2O_4.—When the other oxides are heated in the air, either the trioxide takes up an atom of oxygen or the pentoxide loses an atom with the formation of the more stable tetroxide. It forms no hydroxide.

Antimony Sulphides. — Antimony trisulphide, Sb_2S_3, and antimony pentasulphide, Sb_2S_5. The former occurs in nature as stibnite and is the most abundant compound of antimony found in nature. The natural sulphide is black and the artificial is red. The hydrosulphides are analogous to those of arsenic and tin.

Bismuth Compounds

Bismuth Oxides. — Four oxides are known: Bi_2O_3, Bi_2O_5, Bi_2O_4, and BiO.

The monoxide, BiO, is a brownish powder, oxidizing very readily.

Bismuth Trioxide, Bi_2O_3, occurs naturally and may be prepared by burning bismuth or heating the hydroxide. The hydroxide may be made by adding an alkaline hydroxide to a solution of a bismuth salt. Bismuth forms salts which are readily decomposed by water into basic salts. The basic nitrate and basic carbonate, known as subnitrate and subcarbonate, are white insoluble powders which are used medicinally and as cosmetics.

Bismuth Pentoxide, Bi_2O_5, is obtained by heating metabismuthic acid, $HBiO_3$. This body is formed by passing a current of chlorine through a boiling solution of potassium hydroxide, holding the bismuth trioxide in suspension. Bismuth pentoxide is a very unstable body which forms one hydroxide.

Bismuth Sulphides. — Two sulphides are known, bismuth monosulphide, BiS, and bismuth trisulphide, Bi_2S_3. The latter is found in nature and the other is prepared by precipitation from the solution of a bismuth salt with sulphuretted hydrogen.

Vanadium Trioxide, V_2O_3, is a black powder; and *Vanadium Pentoxide*, V_2O_5, is a brown mass. H_3VO_4, orthovanadic acid, and HVO_3, metavanadic acid, are the acids derived from the pentoxide.

Columbium Pentoxide, Cb_2O_5, with H_3CbO_4, orthocolumbic acid, and *Tantalum Pentoxide*, Ta_2O_5, and orthotantalic acid, H_3TaO_4, show the resemblances among the compounds of the other elements of the group.

EXERCISES

1. Tabulate the hydroxides of phosphorus, arsenic, antimony, and bismuth.

2. What characteristics become more pronounced with the increase of atomic weights in the case of the trioxides of phosphorus, arsenic, antimony, and bismuth?

3. Magnesium ammonium phosphate, when heated, is converted into $Mg_2P_2O_7$. Calculate the percentage of arsenic in magnesium pyroarsenate.

CHAPTER XLIV

GROUP VI

THE OXIDES AND HYDROXIDES OF SULPHUR

THE type oxide of this group is MO_3, but most of its members also form MO_2.

Three oxides of sulphur are recognized: sulphur dioxide, SO_2; sulphur trioxide, SO_3; and sulphur sesquioxide, S_2O_3, about the existence of which there is some doubt.

Sulphur Dioxide, SO_2, occurs in volcanic gases and the gas produced in the combustion of coal carrying pyrites (Chapter XII). It is obtained by the burning of sulphur or pyrites in the air or oxygen: —

$$S + O_2 = SO_2\text{; or } 2\,FeS_2 + 11\,O = Fe_2O_3 + \uparrow 4\,SO_2.$$

In the laboratory it is usually prepared by the action of metals on concentrated sulphuric acid: —

$$Hg + 2\,H_2SO_4 = HgSO_4 + 2\,H_2O + \uparrow SO_2.$$

Sulphur dioxide is a colorless gas with a suffocating odor. It has a specific gravity of 2.2; hence, one liter weighs 2.86 grams. It may be liquefied by cooling to – 15°, or submitting it to a pressure of three atmospheres. The liquid, which has a specific gravity of 1.43, boils at – 8°. It forms a crystalline solid at – 76°. Sulphur dioxide is quite soluble in water, one part of water dissolving 50 volumes. It bleaches organic matter. However, this occurs only in the presence of water and is often transient. It acts as a disinfectant and is particularly efficient in destroying objectionable insects.

Sulphurous Acid, H_2SO_3, is formed by the solution of the dioxide in water: —

$$SO_2 + H_2O = H_2SO_3.$$

It is known only in solution and is decomposed by light. It is a weak dibasic acid, forming two classes of sulphites, normal and acid sulphites, as Na_2SO_3 and $NaHSO_3$. When the sulphites are treated with a strong acid, sulphurous acid is liberated, and it readily breaks up into sulphur dioxide and water.

The *sulphites* of sodium, magnesium, and calcium are used in the preparation of wood pulp in making paper. They are deliquescent and very soluble bodies. The normal sulphites are more easily crystallized and are less soluble. Some of the sulphites are used medicinally. They are strong reducing agents, and are frequently used in photography and in bleaching woolen, silk, and straw goods.

Hyposulphurous Acid, $H_4S_2O_4$, or H_2SO_2, is obtained when sulphurous acid is treated with finely divided zinc. Apparently hydrogen is given off and another portion of the acid reduced: —

$$Zn + H_2SO_3 = ZnSO_3 + H_2; \quad H_2SO_3 + H_2 = H_2SO_2 + H_2O.$$

This acid, which is known only in solution, appears to be derived from the unknown oxide SO. The acid and its salts, *hyposulphites*, are powerful reducing agents.

Sulphur Trioxide, SO_3, is not formed in large quantities by the direct burning of sulphur in the air or oxygen. The dioxide is the main product. Sulphur dioxide takes up one more atom of oxygen by passing the mixed gases over finely divided platinum (Schröder contact process):—

$$SO_2 + O = SO_3;$$

or on treatment of SO_2 with nitrogen trioxide:—

$$SO_2 + N_2O_3 = SO_3 + 2\ NO.$$

It was earlier prepared by heating ferrous sulphate:—

$$2\ FeSO_4 = Fe_2O_3 + SO_2 + SO_3;$$

and later by heating fuming sulphuric acid:—

$$H_2SO_4,\ SO_3 = H_2SO_4 + SO_3.$$

Sulphur trioxide is a colorless liquid which crystallizes when cooled, and dissociates at a red heat. It usually contains a small amount of water and forms long white needles. It absorbs water with avidity, producing great heat. Sulphur trioxide is used to make fuming sulphuric acid, which in turn serves to make 100 per cent acid, and in "sulphonating" carbon compounds. These latter may be high explosives, coal-tar colors, or synthetic medicinal compounds.

Sulphuric Acid, oil of vitriol, H_2SO_4, is probably the most important of all chemicals. On account of its extensive use, immense quantities are made annually; in fact, the commercial progress of a nation may be judged by the amount of sulphuric acid made and used. Over two million tons of sulphuric acid were made in the United States in 1908, whereas ten years ago it was half that amount. It has been found free in a few rivers (Rio Vinagre) and in lake waters which come from volcanic regions.

A little before 1740, Ward, an Englishman, made sulphuric acid by burning sulphur and niter together, and condensing the vapors in a glass vessel containing a little water. The reactions involved in this process are the basis of the method now in use under the name of the "lead-chamber process." The reactions are more or less complicated, but for our purpose may be simplified as follows: —

Sulphur, or iron pyrites, is burned to produce sulphur dioxide: —

$$S + O_2 \rightleftarrows SO_2; \text{ or } 2\ FeS_2 + 11\ O \rightleftarrows Fe_2O_3 + \uparrow 4\ SO_2.$$

This takes place in the sulphur or pyrites burners. If the latter, they are built to burn either lump pyrites or the powdered ore, which is known as "fines."

The sulphur dioxide is oxidized to SO_3: —

$$SO_2 + N_2O_3 = SO_3 + N_2O_2; \text{ or}$$
$$2\ SO_2 + N_2O_4 = 2\ SO_3 + N_2O_2.$$

This is accomplished by first passing the gases over a pot which contains sodium nitrate to which sulphuric acid is added. Nitric acid is evolved, which is reduced to the lower oxides by the sulphur dioxide. The mixture of gases is then passed into large chambers lined with lead. There water in the form of steam is added: —

$$SO_3 + H_2O \rightleftarrows H_2SO_4.$$

The oxides of nitrogen, which are expensive, are used over again; therefore air is introduced. The oxygen re-forms the tri- and tetroxides of nitrogen: —

$$2\ N_2O_2 + O_2 \rightleftarrows 2\ N_2O_3; \text{ or } N_2O_2 + O_2 \rightleftarrows N_2O_4.$$

The nitrogen trioxide combines with more sulphur dioxide, oxygen, and water to form nitrosyl-sulphuric acid, known as "chamber crystals": —

$$2\ SO_2 + N_2O_3 + O_2 + H_2O = 2\ SO_2, OH, NO_2.$$

On addition of water these break up, reforming nitrogen trioxide, which again oxidizes sulphur dioxide: —

$$2\,SO_2, OH, NO_2 + H_2O = 2\,H_2SO_4 + \uparrow N_2O_3.$$

This gas can be and is used over and over again, although there is more or less loss, as a number of other reactions take place. In order to save these oxides of nitrogen as far as possible, the escaping gases are passed through concentrated sulphuric acid, which absorbs the tri- and tetroxides. This is done in a Gay-Lussac tower, essentially a lead-lined stack about three meters square and ten to twenty meters high. This tower is loosely packed with coke, quartz, or other acid-resisting material and is so arranged that there is a steady flow of concentrated sulphuric acid from the top to the bottom. The brown and red oxides are absorbed by the acid and collected in a reservoir. This acid is called "niter acid."

The "niter acid" gives up these oxides when diluted and heated. It is therefore pumped, usually by an "acid egg," to the top of a similar tower, called the Glover tower, which is inserted between the pyrites or sulphur burners and the first chamber. The acid is diluted at the top of the tower and run over the large surface of acid-resisting material inside to the bottom of the tower. The hot gases from the burners enter the tower at the bottom and heat the liquid as it falls. The oxides of nitrogen are swept on into the chambers, where they again perform their functions. At the same time the acid is concentrated by the heat and collects in a reservoir at the bottom, whence it is pumped to the top of the Gay-Lussac tower, to be used over again to absorb the escaping nitrogen trioxide.

Sulphuric acid, condensing inside and on the walls of the lead chambers, collects at the bottom. It is called "chamber acid," and contains from 60 to 78 per cent of sulphuric acid with a specific gravity of from 1.5 to 1.71. "Chamber acid" is quite impure, containing lead, iron, arsenic, and other metals, and the oxides of nitrogen. It is first purified in part by concentrating in cast-iron stills until it has a specific gravity of 1.8 and contains about 80 per cent H_2SO_4. This is commercial "oil of vitriol." It is further purified and concentrated by distillation in platinum stills. The gaseous impurities are swept away by the water, which passes off with some acid; the solid impurities accumulate in the bottom of the still and are drained away; while the purest acid condenses on the sides of the platinum stills, which are cooled by water jackets, and runs off into suitable containers.

Such purified sulphuric acid has a specific gravity of 1.84, and contains about 98.5 per cent acid. It is a colorless, oily liquid which mixes with water in all proportions. When mixed with water, much heat is evolved and there is a contraction in volume. Its great affinity for water causes it to be used extensively as a desiccating agent, especially for drying gases. It removes water from organic matter, upon which fact its powerful corrosive action when brought in contact with living matter is dependent in part. It is very poisonous.

The metals and their oxides are not readily soluble in concentrated sulphuric acid, unless it is heated, when there is a decomposition of the acid (oxidizing action). The cold concentrated acid frequently has little action, due in part, no doubt, to the insolubility of the sulphate formed in the concentrated acid. However, the diluted acid is a good solvent for a number of the metals and oxides: —

$$Fe + H_2SO_4 \rightleftharpoons FeSO_4 + H_2;$$

$$MgO + H_2SO_4 \rightleftharpoons MgSO_4 + H_2O;$$

$$ZnCO_3 + H_2SO_4 \rightleftharpoons ZnSO_4 + H_2O + CO_2.$$

Sulphuric acid is a dibasic acid which forms a large number of important acid, normal, and double salts. These will be considered in the next chapter. There is scarcely any substance used for food, clothing, or shelter which is not directly or indirectly dependent upon sulphuric acid. It is used in immense quantities for making phosphatic fertilizers, coal-tar dyes, medicines, galvanizing and tinning iron, high explosives, many chemicals, as hydrochloric and nitric acids, sulphates, and so forth.

Fuming Sulphuric Acid, $H_2S_2O_7$, is prepared by distilling ferrous sulphate and collecting the sulphur trioxide evolved in concentrated sulphuric acid (Nordhausen acid); or by the solution of sulphur trioxide as it is produced by the contact process in sulphuric acid. When it has a specific gravity of 1.93, it contains 45 per cent of SO_3. It fumes in the air. It is used to dissolve indigo, and in the making of certain dyestuffs and of smokeless powders.

Persulphuric Acid, $H_2S_2O_8$, and the *persulphates,* as $(NH_4)_2S_2O_8$, are made by the electrolysis of a very cold solution. They are strong oxidizing agents.

Thiosulphuric Acid, $H_2S_2O_3$, formerly called hyposulphurous acid, may be looked upon as H_2SO_4, in which an atom of oxygen has been replaced by one of sulphur. Only the salts, thiosulphates, are known. When treated with an acid, they decompose into water, sulphur dioxide, and sulphur: —

$$Na_2S_2O_3 + 2\,HCl \rightleftarrows 2\,NaCl + \uparrow SO_2 + \downarrow S + H_2O.$$

Sodium Thiosulphate is the most important salt. It is prepared by boiling sodium sulphite with sulphur. It has a strong reducing action and is much used in photography as "hypo-solution," since the silver halides are soluble in its water solution. The salt is commercially sold under the old name of sodium hyposulphite, which is a misnomer.

The *Thionic Acids* constitute a series differing in chemical composition by an atom of sulphur. They are $H_2S_2O_6$, $H_2S_3O_6$, $H_2S_4O_6$, and $H_2S_5O_6$. They form salts and are called dithionic, trithionic, and so forth, acids.

EXERCISES

1. How much sulphuric acid (80 per cent) should be made from 5 tons of iron pyrites which carries 44 per cent of sulphur?

2. Complete the following reactions: (*a*) $CuCO_3 + H_2SO_4$; (*b*) $NaNO_3 + H_2SO_4$; (*c*) $H_2S_2O_7 + H_2O$; (*d*) $Mg + H_2SO_4$ (dil.); (*e*) $Al + H_2SO_4$; (*f*) $Zn + H_2SO_4$ (conc.).

CHAPTER XLV

THE SULPHATES. ALUMS

MANY of the sulphates occur naturally in great abundance. Most of them are soluble in water and crystallize well. The most insoluble ones are those of the positive series of Group II, and lead.

The sulphates are formed: —

First, by the action of sulphuric acid upon the metals, oxides or carbonates: —

$$Zn + H_2SO_4 \rightleftharpoons ZnSO_4 + \uparrow H_2,$$

$$CuO + H_2SO_4 \rightleftharpoons CuSO_4 + H_2O,$$

$$Na_2CO_3 + H_2SO_4 \rightleftharpoons Na_2SO_4 + H_2O + \uparrow CO_2;$$

Second, by roasting some of the sulphides, as —

$$PbS + 2\ O_2 = PbSO_4;$$

and

Third, by precipitation, in the case of the insoluble ones: —

$$BaCl_2 + H_2SO_4 \rightleftharpoons \downarrow BaSO_4 + 2\ HCl.$$

SULPHATES OF GROUP I

These are generally white, soluble, crystalline bodies. Copper sulphate, which contains water, however, is blue.

Sodium Sulphate, Glauber's salt, or "sal-mirabile," $Na_2SO_4, 10\ H_2O$, occurs widely distributed in nature, especially in various mineral waters and alkali lands. When made in the Le Blanc soda process, it is called "salt cake," and in the manufacture of nitric acid, "niter cake."

The salt mentioned is stable at temperatures only below + 35°. Above that temperature it melts, separating into a saturated solution of an anhydrous sulphate which alone melts at + 886°; 100 parts of water dissolve 12 parts of Glauber's salt at 0°, 354 at + 34°, and 238 at + 100°. This is accounted for by the formation of different hydrates. It readily forms supersaturated solutions. It is used in medicine, and in the anhydrous form to make low grades of glass.

Potassium Sulphate, K_2SO_4, occurs in the salt beds of Stassfurt. It is extensively used as a fertilizer, especially in the form of a double sulphate, under the name of kainite, which has the formula $K_2SO_4,MgSO_4,MgCl_2,H_2O$. It is also used in making ordinary alum.

Potassium Acid Sulphate, $KHSO_4$, and *Potassium Disulphate*, $K_2S_2O_7$, are white deliquescent solids which are used as a flux in fusing and decomposing minerals.

Copper Sulphate, blue stone, blue vitriol, $CuSO_4, 5\ H_2O$, loses water on heating, and becomes first turquoise blue ($CuSO_4, H_2O$) and then white ($CuSO_4$). On heating higher, copper oxide is formed. It is found in small amounts in nature. Copper sulphate is soluble in water and is poisonous. It is used in electroplating, dyeing, and for an insecticide, as in making Bordeaux mixture, and in purifying water for drinking purposes.

Sulphates of Group II

Magnesium Sulphate, Epsom salts, $MgSO_4, 7\ H_2O$, which occurs in many natural mineral waters and in the German salt deposits, is a white, crystalline, soluble body. It is used medicinally as an aperient.

Calcium Sulphate, gypsum, alabaster, $CaSO_4,2\ H_2O$, also occurs naturally without water, when it is called anhydrite. When heated to + 110° or + 120°, most of the water is driven off and plaster of Paris is formed. This is capable of reabsorbing water and "setting," or hardening. It is therefore used in surgery for bandaging broken bones. Strips of cloth are covered with a milk of plaster of Paris and placed around the limb. As the excess of water evaporates, the $CaSO_4, 2\,H_2O$ forms a stiff support which later must be broken to remove it. In making plaster casts harder, a solution of alum or borax is mixed with the plaster of Paris. More time is then required in the setting. As plaster of Paris is porous, it is often covered with melted paraffine or painted with a solution of paraffine in benzene to render it impervious. Stucco is plaster of Paris mixed with glue. When heated above + 160°, it does not combine readily with water again, and is said to be "dead burned." Plaster of Paris is used as an indirect fertilizer. Prepared artificially (by precipitation with an alkaline sulphate), it is a white powder, slightly soluble in water. When gypsum is dissolved in natural waters, a "permanent hardness" of the water is produced.

Barium Sulphate, heavy spar, "barytes," $BaSO_4$, occurs naturally as a hard crystalline mass. When ground up, it is used to give weight to paper, paint, and so forth. Artificially prepared, it is a heavy, white powder, and possesses distinct value in making paints. There is no objection to its use for this purpose if it is sold under its own name and not as white lead. It is extremely insoluble in water (1 : 350,000).

Zinc Sulphate, white vitriol, $ZnSO_4, 7\,H_2O$, is soluble in water. It is used as an emetic (depressant), yet it is poisonous. It is also used in some forms of galvanic batteries.

Mercuric Sulphate, $HgSO_4$, is a white, soluble, crystalline salt which is used in some batteries, as Clark's standard cell. It usually changes and darkens on exposure to light. It hydrolyzes on standing in water, forming a basic sulphate, $2\,HgO,HgSO_4$.

Mercurous Sulphate, Hg_2SO_4, readily forms basic salts on the addition of water.

SULPHATES OF GROUP III

Aluminum Sulphate, $Al_2(SO_4)_3$, $18\,H_2O$, may be rendered anhydrous by heating, but ordinarily it is a white powder, soluble in water. This sulphate readily combines with the sulphates of the alkali group, molecule for molecule, to form an important class of bodies known as

The Alums. These have the typical formula, $M^{III}{}_2(SO_4)_3$, $N^{I}{}_2SO_4$, $24\,H_2O$, or $M^{III}N^{I}(SO_4)_2$, $12\,H_2O$. M may be equivalent to Al, Fe, Cr, and so forth, and N to Li, Na, K, Rb, Cs, and NH_4, or an organic derivative of ammonium. The name of the trivalent element is prefixed to designate the alum, as for example, *chrom-potassium alum*, $Cr_2(SO_4)_3$, K_2SO_4, $24\,H_2O$.

Potassium Alum, $Al_2K_2(SO_4)_4$, $24\,H_2O$, occurs in nature and has been known for a long time. The pure form is known as Roman alum. It is found dissolved in alum waters and may be made from alum shales (aluminum silicates containing much iron pyrites) by roasting, so that aluminum sulphate or ferrous sulphate is formed. These are dissolved in water, the ferrous sulphate crystallized out on concentration, potassium sulphate then added, and the alum crystallized out on further evaporation. Potassium alum dissolves in eight parts of cold water and one third part of boiling water, from which it may be obtained in fine large crystals. *Ammonium Alum* resembles potassium alum. *Sodium Alum* deliquesces and does not crystallize well.

Properties of the Alums. Potassium and ammonium alum crystallize easily and do not readily absorb water. They are used medicinally, and in the place of aluminum sulphate in tanning and sizing paper, as they have the property of rendering gelatin insoluble. Paper when first made is porous. When treated with glue (gelatin) and an alum solution, and passed between hot rollers, the surface becomes impervious, and ink is not absorbed. The alums are also used as mordants in dyeing. When coloring matters are precipitated with alums, "lake dyes" are obtained. Alums are used in purifying waters for drinking purposes, as they readily hydrolyze in dilute solution. The gelatinous aluminum hydroxide formed incorporates not only the suspended impurities, but many of the substances dissolved in the water. It incorporates a large proportion of the bacteria present and settles as a jelly. The purified water may then be drawn off, or, as is more usual, the jelly is separated by filtration. The alums have been used in making cheap baking powders, but as alum is an astringent, such use is objectionable in foods, as it interferes with the digestive processes.

SULPHATES OF THE REMAINING GROUPS

Lead Sulphate, $PbSO_4$, is a white, quite insoluble, crystalline substance which is used as a pigment in making paints. A basic lead sulphate, $2\,PbO,PbSO_4$, known as "white sublimed lead," is used extensively as a pigment in the place of ordinary "white lead." On account of the insolubility of lead sulphate, the antidote for lead poisoning is a soluble sulphate.

Ferrous Sulphate, copperas, green vitriol, $FeSO_4, 7\,H_2O$, is a green, crystalline substance, soluble in water, and poisonous. It is decomposed by heat. It is used medicinally and as a disinfectant, or rather as a deodorant. It is also used in tanning, dyeing, and making inks.

Ferrous sulphate, as well as the sulphates of other bivalent positive elements, as Mn, Co, Ni, Mg, and so forth, form a series of double salts with the sulphates of the alkali metals with the type formula, $M^{II}N^{I}_2(SO_4)_2$, $6\ H_2O$. These all crystallize in monoclinic tables.

Ferric Sulphate, $Fe_2(SO_4)_3$, is a deliquescent, yellowish solid which is used medicinally.

EXERCISES

1. Tabulate the formulas of the following: soda alum, Roman alum, ammonium-iron, potash-chromium, rubidium-manganese, and cæsium alums.

2. Complete the equations: —

(1) $NaHCO_3 + Al_2K_2(SO_4)_4,\ 24\ H_2O \rightarrow$,
(2) $Na_2SO_4 + Pb(NO_3)_2 \rightarrow$.

CHAPTER XLVI

OTHER OXIDES OF GROUP VI, AND THEIR DERIVATIVES

NEGATIVE SERIES

SO_2	H_2SO_3	SO_3	H_2SO_4
SeO_2	H_2SeO_3	——	H_2SeO_4
TeO_2	H_2TeO_3	TeO_3	H_2TeO_4

Selenium Dioxide, SeO_2, is prepared by burning selenium in the air or by oxidizing it with nitric acid. It forms white crystals which volatilize at +320°, has a peculiar disagreeable odor, and is deliquescent.

The hydroxide, $SeO(OH)_2$, or *Selenious Acid*, H_2SeO_3, is prepared by oxidizing selenium with nitric acid. It is easily reduced, yielding selenium. Selenious acid is dibasic and forms selenites, which are also easily reduced. When heated on charcoal, they give the odor of decayed horseradish.

Selenic Acid, H_2SeO_4, is obtained by the strong oxidation of selenium:—

$$Se + 3\,Cl_2 + 4\,H_2O = H_2SeO_4 + 6\,HCl.$$

It has not been entirely freed from water. It decomposes at +280° into oxygen and selenious acid. It is a colorless, very acid liquid, which forms the selenates, analogous to the sulphates.

Tellurium Dioxide, TeO_2, occurs in nature. *Tellurous Acid*, H_2TeO_3, is a light white powder, slightly soluble in water, which forms tellurites.

Tellurium Trioxide, TeO_3, is obtained by heating telluric acid. It is a yellow, crystalline mass which is decomposed when strongly heated.

Telluric Acid, H_2TeO_4, is prepared by fusing tellurium or tellurium dioxide with potassium carbonate and an oxidizing agent, as potassium nitrate, and setting the acid free by means of a stronger one.

Positive Series

CrO	$Cr(OH)_2$	Cr_2O_3	$Cr_2(OH)_6$	CrO_2	——	CrO_3	$CrO_2(OH)_2$
MoO	——	Mo_2O_3	——	MoO_2	——	MoO_3	$MoO_2(OH)_2$
——	——	——	——	WO_2	——	WO_3	$WO_2(OH)_2$
——	——	——	——	UO_2	$U(OH)_4$	UO_3	$UO_2(OH)_2$

Besides these, there are many compounds of more complicated formulas.

Chromium Monoxide, chromous oxide, CrO, is not known free from water. The hydroxide, $Cr(OH)_2$, is a yellow precipitate produced by adding a soluble hydroxide to a chromous solution, as $CrCl_2$. On the removal of water, the oxide is formed. It is readily oxidized by the oxygen of the air. When the hydroxide is heated it gives off hydrogen: —

$$2\,Cr(OH)_2 = Cr_2O_3 + H_2O + H_2.$$

The chromous salts are obtained by reduction of the chromic compounds, generally by heating in hydrogen. They absorb oxygen with avidity at ordinary temperatures.

Chromium Sesquioxide, chromic oxide, Cr_2O_3, is found in nature as chromic iron ore, Cr_2O_3, FeO. It is the most stable of the chromium oxides, and is prepared artificially by heating the hydroxide, $Cr(OH)_3$. It is a green powder, specific gravity 5.21, and is almost insoluble in acids, especially after intense heating. It is used in coloring glass and porcelain green, and as a green pigment. It does not give as live a color, however, as do the copper arsenites.

Chromium Hydroxide, $Cr(OH)_3$, is precipitated as a gelatinous, greenish blue compound from solutions of trivalent chromium compounds: —

$$CrCl_3 + 3\ NaOH \rightleftarrows 3\ NaCl + \downarrow Cr(OH)_3.$$

It dissolves in an excess of the fixed alkaline hydroxides. This would indicate acidic character, which is more evident when it is partially dehydrated: —

$$Cr(OH)_3 = CrO,OH + H_2O,$$

from which are derived the chromites. For example, if the hydrogen is replaced by iron, we have $Fe(O,OCr)_2$, or FeO,Cr_2O_3, chromic iron stone, chromite, ferrous chromite, the important occurrence in nature. If two molecules of the hydroxide have one molecule of water removed, we have $Cr_2O(OH)_4$, a brilliant green powder, known as Guignet's green, which is used as a pigment. The substance is made commercially by an indirect method and not as stated above.

Chromium hydroxide is soluble in the ordinary acids, by which conduct it exhibits its basic character. The normal chromium salts, as the sulphate, $Cr_2(SO_4)_3$, the chloride, $CrCl_3$, and so forth, are derived from this compound. They are quite stable toward oxygen, and are usually purple or violet in color. The sulphate, $Cr_2(SO_4)_3$, forms alums. They are used in dyeing and tanning. By heating a water solution, which is usually purple, it is changed into a green basic salt, which on standing in the cold changes back to purple.

Chromium Trioxide, CrO_3, is prepared by fusing Cr_2O_3

with an oxidizing agent, as Na_2O_2. A yellow mass of a chromate is obtained which is leached with water. The soluble chromate is decomposed by concentrated sulphuric acid, and the trioxide crystallizes in long red needles on cooling. When heated it melts to a red liquid, being decomposed at + 250°: —

$$2\ CrO_3 = Cr_2O_3 + O_3.$$

It is easily reduced to the sesquioxide by means of organic or other reducing matter. It possesses a powerful oxidizing action, and is often used as an oxidizing agent in an aqueous solution. Mixed with concentrated sulphuric acid it exhibits an extremely powerful oxidizing action. This is very pronounced in the presence of organic matter. The long, red rhombic crystals are deliquescent. With water, in which it is very soluble, it appears to form chromic acid, H_2CrO_4, which is not actually known, but a number of salts are derived from it. The solution has an acid taste and is an astringent. It dyes silk, skin, and wool yellow.

When alkaline hydroxides are added to a water solution of CrO_3, the *Chromates*, M_2CrO_4, and *Dichromates*, $M_2Cr_2O_7$, are formed. They are usually prepared, however, directly from the alums and are used in the preparation of other chromium compounds.

Potassium Chromate, K_2CrO_4, is a yellow, crystalline salt, soluble in water. It is decomposed by strong acids to form dichromates: —

$$2\ K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O.$$

When potassium hydroxide is added to the dichromate, the chromate is re-formed: —

$$K_2Cr_2O_7 + 2\ KOH = 2\ K_2CrO_4 + H_2O.$$

Potassium Dichromate, red chromate of potash, $K_2Cr_2O_7$, is manufactured on a large scale from sodium dichromate: —

$$Na_2Cr_2O_7 + 2\ KCl = K_2Cr_2O_7 + 2\ NaCl.$$

It crystallizes in large, red triclinic prisms, which are soluble at ordinary temperatures in 10 parts of water. When heated it decomposes with the liberation of oxygen: —

$$2\ K_2Cr_2O_7 = 2\ K_2CrO_4 + Cr_2O_3 + O_3.$$

It is used in the manufacture of pigments, in photography, and in galvanic batteries.

Lead Chromate, chrome yellow, $PbCrO_4$, resembles the sulphate in solubility in water. It is extensively used as a pigment. Pigments with intermediate shades from yellow to orange are had with various proportions of the basic chromate $[PbO, PbCrO_4]$, which is orange.

Magnesium Chromate, $MgCrO_4, 7\ H_2O$, has the type of the sulphate, Epsom salts.

When some of the chromates are treated with acids, they form polychromates: —

$$K_2Cr_2O_7 + 4\ H_2SO_4 = Cr_2(SO_4)_3, K_2SO_4 + 4\ H_2O + 3\ O.$$

Chromium Sulphides. Cr_2S_3 is a black substance, prepared by a fusion method. It is not obtained by ordinary precipitation methods. When ammonium sulphide is added to chromium sulphate solution, chromium sulphide is not formed, but the hydroxide: —

$$Cr_2(SO_4)_3 + 3(NH_4)_2S + 6\ H_2O = 3(NH_4)_2SO_4 + Cr_2S_3, \text{ but}$$
$$Cr_2S_3 + 6\ H_2O = 2\ Cr(OH)_3 + 3\ H_2S.$$

Molybdenum Trioxide, MoO_3, is an acid-forming oxide which appears to form molybdic acid, H_2MoO_4. *Lead*

Molybdate, wulfenite, $PbMoO_4$, is an important ore of molybdenum. Molybdic acid resembles chromic and silicic acids in forming polymolybdates, as for example, Na_2MoO_4, $Na_2Mo_2O_7$, $Na_2Mo_3O_{10}$, . . . $Na_2Mo_{10}O_{13}$. It also forms "complex" acids and salts; for example, a brilliant yellow precipitate, with the composition $(NH_4)_3PO_4, 12\,MoO_3, 6\,H_2O$, is produced by bringing soluble molybdate and phosphate solutions together. It is insoluble in nitric acid, but readily soluble in ammonium hydroxide. This complex serves as a satisfactory material to separate the phosphoric acid from iron and aluminum compounds in making analyses of phosphates.

Molybdenum Sulphide, MoS, occurs in nature as molybdenite.

Tungsten Trioxide, WO_3, is a yellow powder which resembles MoO_3 in its chemical conduct. The *tungstates*, as $(FeMn)WO_4$ (wolframite), $CaWO_4$ (scheelite), and $PbWO_4$ (stolzite), are the chief tungsten minerals and appear to be derived from tungstic acid, H_2WO_4. A number of polytungstic acids are known. A derivative of one of them, $K_2W_4O_{12}$, is known as "tungsten bronze." As an illustration of the complexity of some of these substances, the determined formula of one may be given (E. F. Smith): $18\,BaO, VO_2, V_2O_5, 8\,P_2O_5, 60\,WO_3, 150\,H_2O$.

Uranium Dioxide, UO_2, enters into some compounds, as $(UO_2), (NO_3)_2$, *uranyl nitrate*. The uranyl salts exhibit splendid greenish yellow fluorescence.

Uranium Trioxide, UO_3, is acid-forming. Uranic acid, H_2UO_4, forms poly-uranates similar to the poly-compounds of the other members of this series.

Uraninite, pitchblende, U_3O_8, appears to be a uranic uranate, $U(UO_4)_2$.

EXERCISES

1. Complete the reaction : —

$$K_2CrO_4 + Pb(NO_3)_2 \underline{\rightarrow}$$

2. Write the reactions showing the changes from each chromium oxide and hydroxide to the other.

CHAPTER XLVII

OXIDES OF THE NEGATIVE MEMBERS OF GROUP VII

No compound of fluorine with oxygen has yet been obtained. Three oxides of chlorine are known; namely, the monoxide (Cl_2O), the tetroxide (Cl_2O_4, or ClO_2), and the heptoxide (Cl_2O_7). Bromine has not as yet yielded pure compounds with oxygen, although three hydroxy-compounds, or oxyacids, are known. Iodine forms the tetroxide (I_2O_4) and pentoxide (I_2O_5). These compounds and the oxyacids are tabulated below.

Cl_2O	$HOCl$	——	$HOBr$	——	HOI
Cl_2O_3	$HOClO$	——	——	——	——
ClO_2*	——	——	——	I_2O_4	——
Cl_2O_5	$HOClO_2$	——	$HOBrO_2$	I_2O_5	$HOIO_2$
Cl_2O_7	$HOClO_3$	——	$HOBrO_3$	——	$HOIO_3$

When chlorine is brought into contact with freshly prepared dry mercuric oxide, this reaction occurs: —

$$HgO + 2\,Cl_2 = HgCl_2 + Cl_2O.$$

Chlorine Monoxide, Cl_2O, is a reddish yellow gas, with a specific gravity of 3, which is readily condensed to a liquid. Both the gas and the liquid are unstable, exploding on warming. They are powerful oxidizing agents and exhibit their explosive properties when any oxidizable substance,

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* ClO_2 is actually recognized. This may or may not be a mixture of Cl_2O_3 and Cl_2O_5 existing as Cl_2O_4.

such as organic material, is present. The gas is readily soluble in water, forming hypochlorous acid: —

$$Cl_2O + H_2O = 2\,HOCl.$$

Hypochlorous Acid, HOCl, which is known only in a water solution, is best obtained by another reaction, which is referred to below. It is a powerful oxidizing agent, and is one of the most important commercial bleaching agents. The bleaching action of chlorine may be accounted for by the formation of hypochlorous acid, for, in the absence of water, it exhibits only very weak bleaching properties. When chlorine is dissolved in water, a reversible reaction takes place: —

$$Cl_2 + H_2O \rightleftarrows HCl + HOCl.$$

Equilibrium soon occurs. If one of the products is removed, the equilibrium is destroyed and the reaction proceeds, as is usual, in a direction to re-establish the equilibrium. For example, if mercuric oxide, HgO, is present, the HCl combines with it to form $HgCl_2$. Hypochlorous acid, HOCl, is a weak acid, and has practically no action upon the mercuric oxide, hence it remains in solution. Therefore, if we suspend HgO in water and lead in chlorine, this reaction takes place: —

$$HgO + H_2O + 2\,Cl_2 = HgCl_2 + 2\,HOCl.$$

If a dilute solution of an alkaline oxide, essentially alkaline hydroxide, is present, both acids are neutralized: —

$$2\,KOH + Cl_2 = KCl + KOCl + H_2O.$$

A solution of a chloride and hypochlorite in equal molecular proportions is obtained. When KOH is used, the solution is called "eau de Javelle"; when NaOH, "Labarraque's solution," or "chlorinated soda." Both solutions are strong disinfecting and bleaching agents. If chlorine is passed into a solution of limewater or over nearly dry slaked lime, this reaction occurs:—

$$2\,Ca(OH)_2 + 2\,Cl_2 = CaCl_2 + Ca(OCl)_2 + 2\,H_2O.$$

The product is known as "bleaching powder," or "chloride of lime," to which the formula $CaCl(OCl)$ is usually assigned. It is an important article of commerce, as it serves as one of the most convenient means for transporting chlorine. This becomes clearer if we consider the conduct of $HOCl$ under variable conditions.

Hypochlorous acid when heated, especially in sunlight, decomposes:—

$$2\,HOCl = 2\,HCl + O_2.$$

This accounts for the evolution of oxygen from chlorine water when it is exposed to sunlight. The reaction is accelerated by some catalytic agents, as cobalt oxide.

When hypochlorous acid, or a hypochlorite, is mixed with an acid, chlorine is evolved:—

$$HOCl + HCl \rightleftarrows H_2O + Cl_2; \text{ or}$$

$$CaCl(OCl) + H_2SO_4 \rightleftharpoons CaSO_4 + HOCl + HCl; \text{ or}$$

$$2\,CaCl(OCl) + H_2O + CO_2 \rightleftharpoons CaCO_3 + CaCl_2 + 2\,HOCl.$$

The last reaction calls attention to the readiness with which bleaching powder decomposes. It should not be kept in tightly closed casks, as the gases are liberated by this reaction and the vessel is liable to burst. Pure chloride of lime contains about 49 per cent of available chlorine. A good grade contains 25 per cent. It is extensively used for disinfecting and bleaching. In the latter it is more generally applied to vegetable fibers, as it is injurious to silk and wool. In any event, the excess used should be removed by subsequent treatment with an "anti-chlor," such as sodium thiosulphate.

Hypobromous Acid, HOBr, and the *Hypobromites* are prepared in the same manner. They are used for the same purposes as the hypochlorites but to a less extent. Both react with ammonia or substituted ammonia compounds as follows:—

$$3\ NaBrO + 2\ NH_3 \underline{\rightarrow} 3\ NaBr + 3\ H_2O + \uparrow N_2;$$
$$3\ NaBrO + CO(NH_2)_2 \underline{\rightarrow} 3\ NaBr + 2\ H_2O + \uparrow N_2 + CO_2.$$

The last reaction is frequently used to determine the amount of urea [$CO(NH_2)_2$], one of the final products of nitrogenic metabolism of animals, discharged in the urine. The hypobromite solution is made with an excess of sodium hydroxide, which combines with the carbon dioxide generated. The sodium bromide is soluble in the water present. The nitrogen is not dissolved, so it is collected and measured.

When solutions of hypochlorous or hypobromous acids are concentrated, or their salts heated, a part is oxidized and a part reduced:—

$$3\ HOCl = HOClO_2 + 2\ HCl, \text{ or}$$
$$3\ KOCl = KOClO_2 + 2\ KCl.$$

The *Chlorates*, as $KClO_3$, salts of *Chloric Acid*, $HOClO_2$, may be made by passing chlorine into a concentrated solution of caustic potash warmed to about +90°:—

$$3\ Cl_2 + 6\ KOH = 5\ KCl + KClO_3 + 3\ H_2O.$$

Potassium Chlorate, $KClO_3$, the most important chlorate, crystallizes out from the above solution first in large, white tabular crystals. Technically, calcium chlorate is usually made first and that treated with potassium chloride:—

$$Ca(ClO_3)_2 + 2\ KCl = CaCl_2 + 2\ KClO_3.$$

It is also made now by electrolysis of a solution of potassium chloride. It has a cool, astringent taste; it is used medicinally, in the preparation of oxygen, and in explosives. When a chlorate is heated, or pulverized with organic or combustible matter, it undergoes rapid decomposition. This has frequently resulted in violent explosions, hence the utmost care should be exercised in handling chlorates.

Chloric Acid, $HClO_3$, is obtained by the action of sulphuric acid upon barium chlorate:—

$$Ba(ClO_3)_2 + H_2SO_4 \underline{\rightarrow} \downarrow BaSO_4 + 2\ HClO_3.$$

The liquid must be concentrated under diminished pressure, as it decomposes above +40°. A 40 per cent solution has a specific gravity of 1.28. This acid and the chlorates are decomposed by hydrochloric acid:—

$$HClO_3 + 5\ HCl = 3\ H_2O + 3\ Cl_2.$$

Chloric acid would appear to be the hydroxide derived from Cl_2O_5:—

$$Cl_2O_5 + H_2O = 2\ HClO_3;$$

but when a chlorate is treated with cold concentrated sulphuric acid, a heavy, dark yellow gas is obtained, which may be condensed to a brown-red liquid. This is known as *chlorine tetroxide*, Cl_2O_4, or ClO_2. The liquid becomes a solid at −79° and boils at +10°. It has a peculiar odor, and when heated to +30° explodes. It is a powerful oxidizing agent, setting fire to sugar or similar organic matter as soon as they come in contact.

As has been suggested, Cl_2O_4 may really be a compound or mixture of Cl_2O_5 and Cl_2O_3, for when dissolved in water this reaction takes place:—

$$Cl_2O_4 + H_2O = HClO_3 + HClO_2.$$

Chlorous Acid, $HClO_2$, may also be formed by dissolving Cl_2O_3 in water:—

$$Cl_2O_3 + H_2O = 2\ HClO_2.$$

Certain salts as $AgClO_2$ and $Pb(ClO_2)_2$ are known.

If an organic substance, such as oxalic acid, $H_2C_2O_4$, is present during the production of chloric acid by the method given, a green gas with a very pungent, irritating odor is generated. This is *Chlorine Trioxide*, Cl_2O_3, which is very unstable, being decomposed by heat, light, or organic matter.

Bromic Acid, $HBrO_3$, and the *Bromates* are prepared in the way that the corresponding chlorine compounds are made, except that no bromine oxides are known.

If iodine is treated with a strong oxidizing agent, it changes into a white powder, known as *Iodine Pentoxide*, I_2O_5. On heating, this decomposes into iodine and oxygen, hence it possesses strong oxidizing properties. It dissolves in water to form iodic acid:—

$$I_2O_5 + H_2O = 2\ HIO_3.$$

Iodic Acid forms salts, as sodium iodate, $NaIO_3$, which sometimes are found in natural beds of sodium nitrate. The acid has strong oxidizing and bleaching properties. It serves to show the influence temperature and concentration play in the rate of reactions. When water solutions of iodic acid and sulphur dioxide are mixed, this reaction occurs:—

$$2\ HIO_3 + 5\ SO_2 + 4\ H_2O = 5\ H_2SO_4 + I_2.$$

Free iodine colors starch blue; therefore, if a few drops of a starch solution are added, the moment the reaction occurs the colorless solutions become blue. If proper amounts of solutions of definite strength are taken, the actual time for the reaction is regular for each experiment.

The time changes with the change of strength or the temperature.

Perchloric Acid, $HClO_4$, is formed by the decomposition of chloric acid: —

$$2\,HClO_3 = HClO_2 + HClO_4.$$

It is usually prepared by treating barium perchlorate with sulphuric acid: —

$$Ba(ClO_4)_2 + H_2SO_4 = BaSO_4 + 2\,HClO_4.$$

It is a mobile, colorless liquid, with a specific gravity of 1.78. It can be preserved but a short time, and then only in the dark. It is a powerful oxidizing agent, and sets fire to paper and wood at once, and causes severe wounds when brought in contact with the skin. It appears to be the hydroxide of *chlorine heptoxide*, Cl_2O_7, about the existence of which there is some question.

When potassium chlorate is heated just to fusion, a decomposition occurs as follows: —

$$2\,KClO_3 = KClO_4 + KCl + O_2.$$

The *Perchlorates* are sometimes found in natural niter, but it should be removed before the nitrate is applied as fertilizer, for it is injurious to plants. On treating perchloric acid with iodine the chlorine is displaced: —

$$HClO_4 + I = HIO_4 + Cl.$$

Periodic Acid, HIO_4, is a colorless, crystalline, deliquescent solid. It decomposes when heated to + 140° and possesses a powerful oxidizing action. The periodates are prepared by heating the iodates.

EXERCISES

1. Arrange in tabular form the properties of the oxides and hydroxides of chlorine.

2. Contrast the conduct of chlorine, bromine, and iodine with the hydrogen and the hydroxy-compounds of those elements.

CHAPTER XLVIII

OXIDES AND SULPHIDES OF MANGANESE

MANGANESE resembles chromium and iron not only in physical properties, but in the number and variety of its oxygen compounds and their derivatives as well. There are also striking resemblances between some of its compounds and some of the halogen compounds. This is especially the case in the number and variety of the oxygen compounds of manganese and chlorine, and the resemblance in chemical conduct of their derivatives.

Manganese shows greater variation in valence towards oxygen than any other element known. It forms MnO, Mn_3O_4, Mn_2O_3, MnO_2, MnO_3, and Mn_2O_7. The monoxide and sesquioxide are base-forming; the last two are acid-forming, while the dioxide is weakly so; and Mn_3O_4 may be regarded as neutral; it is the most stable. Some of the oxides occur in nature and constitute the main sources of manganese.

Manganese Monoxide, MnO, is obtained by heating the higher oxides in hydrogen. It is a stable, greenish powder which forms manganous salts with acids; for example, $MnCl_2$, $Mn(NO_3)_2$, and $MnSO_4$. These are the chief salts containing manganese as a base. As a rule, they are pink colored and stable in acid solutions, but absorb oxygen readily in the presence of alkalies. The sulphate ($MnSO_4$), nitrate [$Mn(NO_3)_2$], and chloride ($MnCl_2$) are stable, crystalline compounds.

When solutions of these salts, for they are all soluble in water, are treated with an alkaline hydroxide, this reaction takes place:—

$$MnCl_2 + 2\ NaOH \rightarrow 2\ NaCl + \downarrow Mn(OH)_2.$$

Manganous Hydroxide, $Mn(OH)_2$, is a white gelatinous compound which rapidly becomes brown on exposure to air, due to oxidation.

Manganese Sesquioxide, manganic oxide, Mn_2O_3, occurs in nature as braunite. With dilute hydrochloric acid it forms $MnCl_2$, and MnO_2 is produced. If the acid is concentrated, all of the manganese forms $MnCl_2$, and Cl_2 is evolved. With fairly concentrated sulphuric acid, it forms the manganic salt, $Mn_2(SO_4)_3$, which is purple-red in color.

When these are precipitated from a water solution by an alkaline hydroxide, a brown-red hydroxide is obtained:—

$$Mn_2(SO_4)_3 + 6\ NaOH \rightarrow 3\ Na_2SO_4 + 2\ Mn(OH)_3.$$

This hydroxide readily loses a molecule of water, and MnO, OH is formed. This brown compound is found in nature as manganite and resembles metaluminic acid in its conduct.

Manganous-manganic Oxide, Mn_3O_4, occurs in nature as hausmannite. It is produced when any of the oxides are heated in the air. It gives no salts with acids nor does it form an oxyacid. It may be looked upon as the manganese salt of metamanganous acid, $Mn(OMnO)_2$, or the manganese salt of orthomanganic acid, Mn_2MnO_4, as it shows no resemblance to the spinels.

Manganese Dioxide, black oxide of manganese, MnO_2, occurs in nature as the mineral pyrolusite. It occurs widely distributed and in fair amounts, but in pockets, hence the extent of a deposit cannot be foretold. It is the chief ore of manganese. It is formed when oxidizing agents are added to the manganous salts in solution. It is used in preparing oxygen and chlorine, as a depolarizer in Leclanché cells, and in "bleaching" and coloring glass (washing by fire). It combines with certain positive oxides to form manganites; a complicated one is $K_2Mn_5O_{11}$. They are very little understood, however.

Manganic Acid, H_2MnO_4, would correspond to the trioxide, MnO_3, but no such compound is known to exist in the pure form. Nor is the acid known in the free state. Its compounds, as the manganates, for example, Na_2MnO_4, are prepared by fusing the dioxide with an alkaline hydroxide and some oxidizing agent, as potassium chlorate or sodium dioxide. These compounds are unstable, unless a large excess of alkali is present. The alkaline manganates give a green solution in water, which is decomposed by carbon dioxide or by dilution on exposure to the air. They are strong oxidizing agents, and are used as disinfectants. When a dilute acid is added to the green solution, it becomes pink, due to the formation of the permanganate, $NaMnO_4$. Carbon dioxide produces the same change.

Manganese Heptoxide, Mn_2O_7, is obtained by adding cold concentrated sulphuric acid to potassium permanganate. It is a dark oily liquid, very unstable, which decomposes violently on warming or on coming in contact with organic matter, in the same way that the oxides of chlorine do.

Permanganic Acid, $HMnO_4$, may be prepared by adding dilute sulphuric acid instead of the concentrated acid used in the last reaction. It is a red liquid which is decomposed by heat and organic matter. It is a powerful oxidizing agent, whose chief salt is potassium permanganate, $KMnO_4$. This is prepared from potassium manganate by passing carbon dioxide through a solution of it, which changes from green to red. On evaporation of the solution, dark purplish red crystals are obtained which dissolve in water and give a purple or pink solution. It is a powerful oxidizing agent, and is used as a disinfectant. The permanganates correspond to the perchlorates.

When a permanganate is mixed with dilute sulphuric acid in the presence of oxidizable matter, the permanganate is decomposed with the liberation of oxygen and the loss of the characteristic color: —

$$2\,KMnO_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 3\,H_2O + 5\,O.$$

If iron sulphate, in the ferrous form, is present, it is at once oxidized to the ferric condition: —

$$2\,KMnO_4 + 10\,FeSO_4 + 8\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 5\,Fe_2(SO_4)_3 + 8\,H_2O.$$

This reaction is extensively used to determine the amount of iron in a solution of unknown strength. Permanganates are also decolorized by sulphur dioxide, hydrogen dioxide, and oxalic acid: —

$$2\,KMnO_4 + 5\,SO_2 + 2\,H_2O = K_2SO_4 + 2\,MnSO_4 + 2\,H_2SO_4;$$

$$2\,KMnO_4 + 5\,H_2O_2 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 8\,H_2O + 5\,O_2;$$

$$2\,KMnO_4 + 5\,C_2H_2O_4 + 3\,H_2SO_4 = K_2SO_4 + 2\,MnSO_4 + 10\,CO_2 + 8\,H_2O.$$

Two *sulphides* of manganese, MnS and MnS_2, are found in nature. The monosulphide is flesh-colored and is formed by precipitating a manganous salt solution by an alkaline sulphide: —

$$MnCl_2 + (NH_4)_2S \rightleftarrows 2\,NH_4Cl + \downarrow MnS.$$

A three-fourths sulphide, Mn_3S_4, corresponding to the neutral oxide, Mn_3O_4, is also known.

EXERCISES

1. Complete the reaction for $x\text{Mn}_2\text{O}_3 + y\text{HCl} = w\text{MnCl}_2 +$

2. Complete the equation: $x\text{Mn}_3\text{O}_4 + y\text{HCl} = w\text{MnCl}_2 +$

3. How many cubic centimeters of a solution of potassium permanganate, which contains 40 grams to the liter, would be necessary to oxidize 0.5 gram of iron from the ferrous to the ferric condition?

4. How much iron is present in a solution which requires 47 c.c. of a $\frac{M}{4}$ solution of $KMnO_4$ to produce a pink color?

CHAPTER XLIX

OXIDES AND SULPHIDES OF GROUP VIII

THE oxides of this group are given in tabular form below:

—	FeO	Fe_2O_3	Fe_3O_4	—	(FeO_3)	—	—
—	CoO	Co_2O_3	Co_3O_4	—	—	—	—
—	NiO	Ni_2O_3	—	—	—	—	NiO_4
—	RuO	Ru_2O_3	—	RuO_2	(RuO_3)	Ru_2O_7	RuO_4
—	RhO	Rh_2O_3	—	RhO_2	—	—	—
Pd_2O	PdO	—	—	PdO_2	—	—	—
—	—	Sm_2O_3	—	—	—	—	—
—	—	Eu_2O_3	—	—	—	—	—
—	—	Gd_2O_3	—	—	—	—	—
—	OsO	Os_2O_3	—	OsO_2	OsO_3	—	OsO_4
—	IrO	Ir_2O_3	—	IrO_2	—	—	—
—	PtO	Pt_2O_3	—	PtO_2	—	—	—

It will be noted that, although the type oxide of this group is MO_4, only three have been obtained, and these are quite unstable. Two-thirds oxides, M_2O_3, are known for all of them with the exception of palladium. Monoxides, MO, are known for all except those of the gadolinite subgroup. The two platinum subgroups form MO_2. Salts (-ous) are derived from the monoxides, as cobaltous chloride ($CoCl_2$) and platinous chloride ($PtCl_2$). Salts (-ic) are had from the sesquioxides of the iron and gadolinite subgroups, as ferric chloride ($FeCl_3$) and europic chloride ($EuCl_3$); and from the dioxides of the platinum subgroups, as palladic chloride ($PdCl_4$) and platinic chloride ($PtCl_4$).

Ferrous Oxide, FeO, is prepared by heating ferric oxide with hydrogen at $+500°$. It is a black powder which readily takes up oxygen.

Ferrous Hydroxide, $Fe(OH)_2$, is obtained by the precipitation of a ferrous salt by an alkaline hydroxide as a gelatinous white solid, which is usually seen with a dirty green color. In its preparation it is necessary to exclude oxygen, as it is readily oxidized from the green to the red-brown ferric hydroxide. It forms a series of ferrous salts, the sulphate, $FeSO_4, 7\,H_2O$, copperas, being the most important one. It forms double salts, as $FeSO_4, (NH_4)_2SO_4, 6\,H_2O$ (Mohr's salt), which is used in making ink and dyes.

Ferric Oxide, iron sesquioxide, Fe_2O_3, occurs naturally as hematite, the most important ore of iron. It is found as a powder, mixed with more or less clay as red ocher. It is formed by heating the hydroxide or any salt of iron in which the acid is volatile. When made by heating the sulphate, it was called calcothar and Venetian red. It is a heavy, brownish red powder, insoluble in water and difficultly soluble in acids, especially after it has been ignited. In compact form, as when made by burning pyrites or igniting the natural hydrated oxide, it is known as ruddle. The cinder from the burning of pyrites is largely Fe_2O_3. In addition to its enormous use for making iron, some forms are used as "mineral paint," and others for polishing steel, glass, and so forth.

Ferric Hydroxide, $Fe(OH)_3$, is a reddish brown precipitate produced by the addition of an alkaline hydroxide to a ferric salt, as $Fe_2(SO_4)_3$: —

$$Fe_2(SO_4)_3 + 6\,NaOH \rightarrow 3\,Na_2SO_4 + \downarrow 2\,Fe(OH)_3.$$

This is only one of the several hydroxides which are known more or less and which occur in nature under the names of brown hematite, limonite, goethite, and impure bog iron ore. Mixed with clay, they give yellow ocher and constitute the coloring matter of many soils. Red ocher may be made by heating the yellow ocher. Iron rust is a mixture of these hydroxides. The normal hydroxide, $Fe(OH)_3$, when freshly made, is soluble in acids, giving ferric salts. It is quite soluble in a ferric chloride solution. The chloride may be separated by dialysis, a blood-red colloidal solution of the hydroxide remaining behind. The solution is known as "dialyzed iron" and is used in medicine. On heating the solution, or on the addition of an electrolyte, the hydroxide is precipitated.

We may look upon $Fe(OH)_3$, after it has been partially dehydrated, as having the formula FeO, OH. This combines directly with several oxides, as those of calcium, magnesium, iron, and zinc, whereby are derived the minerals franklinite [$Zn(FeO_2)_2$] and magnetite [$Fe(FeO_2)_2$].

Ferrous-ferric Oxide, magnetic oxide, Fe_3O_4, occurs in nature as magnetite, or "lodestone." It usually contains some titanium. It is prepared in the laboratory by the union of iron and oxygen at high temperatures, as in the case of iron burning in oxygen or at the blacksmith's forge, when it is spoken of as "blacksmith scales." It is a magnetic, neutral oxide from which no compounds are directly derived. It is found as black particles in many sands, from which it is easily separated by a magnet.

Ferric Acid, H_2FeO_4, would correspond to the oxide FeO_3, but no such oxide is known, nor is ferric acid known in the free state. Some of its compounds, however, are known, for when ferric hydroxide is suspended in an alkaline solution and is oxidized by chlorine, a purple solution is obtained from which K_2FeO_4 may be precipitated.

Potassium Ferrate, K_2FeO_4, is also prepared by the fusing of iron with an oxidizing agent, as potassium nitrate.

Cobaltous Oxide, CoO, is prepared by reducing the higher oxides by means of hydrogen. It is a brown powder insoluble in water but soluble in acids, and forms cobaltous compounds, which are the principal salts of cobalt. The silicate, "smalt," is largely used in making blue glass and as a blue pigment. The other chief salts are the nitrate, sulphate, and chloride, which, as a rule, are red, deliquescent bodies becoming blue when deprived of water. They are used as a basis of sympathetic ink.

The *Hydroxide*, $Co(OH)_2$, is obtained by precipitation with an alkaline hydroxide in the absence of oxygen.

Cobaltic Oxide, Co_2O_3, is obtained as a dark brown powder by heating the nitrate. When heated with aluminium oxide, a cobalt ultramarine, or Thénard's blue, is prepared. If zinc oxide is used, a green cinnabar, or Rinmann's green, is obtained.

The *Hydroxide*, $Co(OH)_3$, can be obtained by the precipitation of cobalt salts with oxidizing agents. It is slightly basic, giving a few salts.

Cobaltous-cobaltic Oxide, Co_3O_4, is obtained as black oxide when other cobalt oxides are heated in the air.

Indications point to the existence of cobaltic acid, similar to ferric acid. Potassium cobaltate seems to be formed by fusing any of the oxides with caustic potash.

Nickel Monoxide, NiO, occurs in nature. It is prepared as a green powder by strongly heating the *hydroxide*, $Ni(OH)_2$, which is precipitated by alkaline hydroxides from the solution of a nickelous salt.

Nickel Sesquioxide, Ni_2O_3, is obtained as a black powder by gently heating nickel nitrate in the air. It is soluble in sulphuric and nitric acids, when oxygen is evolved, and in hydrochloric acid, when chlorine is given off. This behavior is characteristic of certain peroxides, as manganese and lead dioxides.

The *Hydroxide*, $Ni(OH)_3$, is formed similarly to the cobalt compound. *Nickel Tetroxide*, NiO_4, is said to exist also.

The *Sulphides* of the iron subgroup as a rule correspond quite closely to the lower oxides, for example, CoS, NiS, and FeS. Sulphides higher than the disulphides, however, are not known.

Ferrous Sulphide is a black substance and is used for generating H_2S. It is usually made for that purpose by fusing the metal and sulphur together. It may also be obtained by the addition of ammonium sulphide to a ferrous salt: —

$$FeSO_4 + (NH_4)_2S \rightleftarrows (NH_4)_2SO_4 + FeS.$$

Iron Disulphide, pyrites, fool's gold, FeS_2, usually occurs as a lustrous or yellow-colored substance of variable crystalline forms, with a specific mineralogical name for each. Some of the crystals are almost perfect. It is chiefly used on account of the sulphur contained in it. Iron forms several other sulphides which occur in nature, as Fe_7S_8 or $Fe_{15}S_{16}$, known as pyrrhotite. This frequently contains copper and nickel and cobalt which give the ore value. The percentage of sulphur may be as high as that in some pyrites, which are burned to make sulphuric acid, but it does not answer for that purpose without auxiliary heat. The ratio of the iron and sulphur is the important factor.

A few *Selenides* occur in nature, generally accompanying the sulphides. The *Tellurides* are generally rarer than the selenides. Both show analogy to the sulphides.

A review of the oxides of the remaining members of this group would be even more technical than those already considered. Attention may be directed to just one; namely, *Osmium Tetroxide*, OsO_4, often improperly called osmic acid. It is used to a certain extent in staining tissue which is to be examined microscopically. It is easily decomposed to a lower black oxide by organic matter.

EXERCISES

1. Show the resemblance of magnetite to the spinel group of minerals.

2. Compare the graphic formulas for the three-fourths oxides of the iron subgroup.

CHAPTER L

BINARY COMPOUNDS OF GROUPS IV AND V

CARBIDES

WHEN carbon is heated with a metal, a carbide is formed. This also occurs in part when the oxide is heated with carbon when it is first reduced to the metal. The ease and extent of the formation depends upon the metal and temperature. In 1808, Davy described potassium carbide, the first carbide recorded. In 1862, Wöhler made an impure calcium carbide by direct synthesis. Although it was known that the carbon in white iron existed there as a carbide, it required the use of the heat of the electric furnace to open the field of this unique class of substances to investigation. Moissan prepared the carbides of many metals by this means.

Many carbides are decomposed by water, giving the oxide or hydroxide of the metal and a hydrocarbon. Some are attacked only by acids, others by alkaline hydroxide solutions, and still others are among the most resistant compounds known. The gaseous hydrocarbons given off by the action of water or acids upon the carbides are methane and acetylene in the main. Methane is produced from Al_4C_3 and acetylene from CaC_2. Thorium and uranium carbides (ThC_2 and U_2C_3) produce gaseous, liquid, and solid hydrocarbons. One of the explanations offered (by Mendelejeff) to account for the existence of natural gas and oil, presupposes the existence of a variety of carbides within the earth, which are decomposed to form a mixture of hydrocarbons when water comes in contact with the carbides.

Some carbides, as those of iron, are dissolved in the solid metal (solid solution) and give to it such peculiar properties as one observes in some cast iron and steels. Of the number of carbides known, the following are at present the most important: —

Calcium Carbide, CaC_2, first prepared commercially in 1894, is made by fusing limestone and carbon (as coke, charcoal, or coal) together in an electric furnace: —

$$CaO + 3\,C = CaC_2 + CO.$$

It is a brilliantly lustrous crystalline solid which decomposes in the presence of water with the evolution of acetylene: —

$$CaC_2 + 2\,H_2O = \uparrow C_2H_2 + Ca(OH)_2.$$

This is the reaction when the carbide is pure. However, the lime and coke are liable to contain phosphorus, sulphur, and silicon compounds, when phosphine, hydrogen sulphide, and hydrogen silicide are generated also. The main use of calcium carbide is for the generation of acetylene, but it is also used in making cyanamide and in desiccating liquids.

Boron Carbide, B_6C, is one of the most stable and hardest known compounds. It is nearly as hard as the diamond; in fact, the powdered crystals may be used to polish some diamonds. BC has also been prepared.

Silicon Carbide, carborundum, SiC, is made by heating to about 2500°, by means of an electric current (process of Acheson), a mixture of quartz sand and coke, with a little salt. Large carbon electrodes are so placed that the current will follow a connecting core of carbon, which is surrounded by the mixture, and heat it. After the current has passed awhile, the core becomes surrounded by a mass of brilliant iridescent crystals of SiC. Carborundum ordinarily resists the action of chemicals, but it is decomposed by alkalies. It is used to line the walls of puddling furnaces in making steel. It is very hard, owing to which property it is used extensively as an abrasive material. It is as hard as the ruby, but not so hard as the diamond. By partially removing the oxygen from SiO_2, *Siloxicon*, SiOC, is produced. SiC_2 has also been prepared.

Iron Carbide, cementite, Fe_3C, is made in the smelting of iron ore by the blast furnace. When cast iron or steel is dissolved in hydrochloric acid, hydrogen and methane are evolved. Perhaps other iron carbides exist, but none has been separated. Nearly pure iron is called ferrite. A mixture of that and the cementite is called pearlite. Micro-photographs of different irons show a variety of crystals, which are attributed to various mixtures to which the terms sorbite, martensite, and troostite are applied by the metallurgist.

NITRIDES

The *Nitrides*, a few of which are known, are usually made by direct union of the element with nitrogen or by heating the element in an atmosphere of ammonia. If made by either method, the nitrogen appears to retain its trivalent character. For example, lithium combines with nitrogen at ordinary temperatures to form lithium nitride, Li_3N. When magnesium is heated in an atmosphere of nitrogen, Mg_3N_2 is produced. This reaction is utilized in separating nitrogen from argon in the air. When calcium is burned in the air, Ca_3N_2 is produced along with the oxide. These reactions are facilitated by the presence of some substance which prevents the oxidation of the metal. For example, if magnesium is heated in the presence of calcium carbide in an electric furnace, the nitrides Mg_3N_2 and Ca_3N_2 are formed. As a rule the nitrides are decomposed by water with the production of ammonia. Boron nitride was one of the earliest nitrides known. When heated with water in the form of steam, it is decomposed: —

$$BN + 3\,H_3O = B(OH)_3 + NH_3.$$

As a matter of fact, the ammonia neutralizes a part of the boric acid. The existence of boron nitride within the earth has been offered as an explanation for the presence of boric acid in the waters of some lakes, which usually contain some ammonia.

If sodium or potassium is heated in an atmosphere of ammonia, one hydrogen atom is replaced by the alkali metal, and $NaNH_2$, sodamide, or KNH_2, potassamide, results. They are decomposed by water: —

$$NaNH_2 + H_2O = NaOH + NH_3.$$

Many phosphides, arsenides, and antimonides are known. They are made by the direct union of the elements. As the last two partake of a metallic character, their compounds will be considered under the head of alloys.

EXERCISES

1. Suppose phosphine and hydrogen sulphide are evolved when impure calcium carbide is treated with water; write the reactions.

2. The specific gravity of acetylene (C_2H_2) is 0.9. What volume would be occupied, at + 20° and 750 mm., by the gas generated from 480 grams of calcium carbide, 95 per cent pure?

CHAPTER LI

COMPOUNDS OF CARBON AND NITROGEN

Carbon and nitrogen do not unite at ordinary temperatures, but there is union when a discharge of electricity occurs between carbon poles in an atmosphere of nitrogen. They combine at high temperatures in the presence of alkalies with the formation of alkaline cyanides, as potassium cyanide, KCN. From this may be made mercuric cyanide, $Hg(CN)_2$, which on heating yields a gas, *cyanogen*, $(CN)_2$: —

$$Hg(CN)_2 = Hg + (CN)_2.$$

It is a colorless gas, very poisonous, and easily condensed to a liquid. It is insoluble in water and burns with a purple flame. Its structure is probably $N \equiv C - C \equiv N$. It acts in a measure like a molecule of chlorine, for we have numerous compounds in which CN enters as if it were an element like chlorine.

Hydrogen Cyanide, HCN, is a colorless liquid, b.-p. $+26.5°$. It is prepared by treating a cyanide with an acid: —

$$KCN + H_2SO_4 \underline{\rightarrow} KHSO_4 + \uparrow HCN.$$

The gas in a very dilute state has the odor of bitter almonds. It is one of the most poisonous substances known, a breath of it being sufficient to produce death; hence the utmost caution should be exercised in working with it. It is very soluble in water, the solution being called hydrocyanic or prussic acid. It is, however, a very weak acid, scarcely reddening blue litmus, while some of its salts are decomposed by the carbon dioxide and water of the atmosphere. It is found in nature in combination in amygdalin, which is a constituent of some leaves, and of the kernels of certain stone fruits and of bitter almonds.

As we secure HCN similar to HCl, so we may obtain CNCl, cyanogen chloride. These compounds may be written graphically as follows: —

$$N \equiv C - C \equiv N, \qquad H - C \equiv N, \qquad Cl - C \equiv N.$$

We have learned that $-NH_2$ acts in the same way, so we may obtain $H_2N - C \equiv N$, which is known as cyanamide.

Wherever we have the group $- C \equiv N$, especially in compounds of carbon, and boil the compound with water and an alkali, there is decomposition with the liberation of ammonia: —

$$R - C \equiv N + H_2O + KOH \rightarrow R - COOK + NH_3.$$

R indicates any element or radical. The potassium forms a salt of an organic acid. This is a very important reaction, as one may learn who studies the compounds of carbon. Recently it has assumed much practical importance, for it has been learned that when nitrogen is brought into contact with molten calcium carbide, a compound known as calcium cyanamide, $CaCN_2$, is formed. This on being treated with water decomposes: —

$$CaCN_2 + H_2O = Ca(OH)_2 + H_2CN_2.$$

And as the cyanamide is produced in the presence of an alkaline hydroxide, it is decomposed with the liberation of ammonia, hence the substance may be used in fertilizers. These reactions may solve in part the difficult problem of fixing nitrogen from the air and rendering it immediately available as plant food.

A number of cyanides are derived from prussic acid, many of them being quite stable and useful.

Potassium Cyanide, KCN, is obtained by heating potassium ferrocyanide [$K_4Fe(CN)_6$] with an alkaline metal to decomposition and dissolving the cyanide formed in water: —

$$K_4Fe(CN)_6 + 2\,K = 6\,KCN + Fe.$$

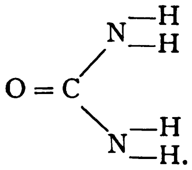
On evaporating the solution, the cyanide is obtained as a white solid which is easily decomposed by acids. It can be fused without decomposing. The fused salt has a strong affinity for oxygen, hence it is a strong reducing agent. This is shown when an easily reduced metallic oxide, like PbO, is stirred into the fused KCN. The molten metal collects in the bottom of the vessel, usually an iron crucible, and *potassium cyanate* floats above: —

$$PbO + KCN = Pb + KCNO.$$

The potassium salt on treatment with an acid is converted into *cyanic acid*, the formula for which may be written graphically in two ways, namely: —

$$H - O - C \equiv N \text{ and } H - N = C = O.$$

In the latter arrangement we have the formula for *isocyanic acid.* If a water solution of the ammonium salt of this acid, ammonium isocyanate, NH_4NCO, is evaporated to secure crystallization, crystals are obtained, to be sure, but not of that compound. The substance contains the same elements in the same proportions, and has the same molecular weight, CON_2H_4, but it is known as *urea,* and may be written graphically as follows: —



This substance occurs in the urine. Up to 1826 it was thought that a special "vital force" brought about the changes observed in compounds in living things, animal and vegetable. As the cyanates may be made directly from the inert elements and by simple treatment may be converted into a product of an animal, it became apparent that the same general laws govern chemical changes whether they occur in living or dead matter. This most important generalization was made by Wöhler, who learned this method for preparing urea in the year referred to.

The oxygen in the cyanates may be replaced by sulphur, when a thiocyanate results, as *potassium thiocyanate*, $KCNS$, for example. This substance in a water solution gives a red color with ferric, but not with ferrous, salts. It is one of the most delicate reactions known.

Many important compounds are prepared from the cyanates and thiocyanates, which are fully considered in organic chemistry.

Some of the metallic cyanides are insoluble in water; for example, when a solution of potassium cyanide is added to a silver nitrate solution, a precipitate of silver cyanide is obtained: —

$$KCN + AgNO_3 \rightleftarrows KNO_3 + \downarrow AgCN.$$

On the addition of another molecule of KCN, the silver cyanide dissolves, due to the formation of a double cyanide, $AgCN, KCN$. The same reaction occurs with gold. This conduct is of great commercial importance, as these solutions are used in silver and gold plating, and for the extraction of gold and silver from their ores. If an acid, as hydrochloric acid, is added to the solution, the double cyanide is decomposed, free HCN is produced, and the silver cyanide is reprecipitated.

If nickel, cobalt, and iron salts are used, one obtains $Ni(CN)_2, 2\,KCN$; $Co(CN)_2, 4\,KCN$; $Fe(CN)_2, 4\,KCN$, and $Fe(CN)_3, 3\,KCN$. One may write these formulas as follows: $K_2Ni(CN)_4$, $K_4Co(CN)_6$, $K_4Fe(CN)_6$, and $K_3Fe(CN)_6$. If an acid is added to these solutions, they are not decomposed with the liberation of HCN, as in the cases referred to above, but the potassium is replaced by hydrogen; for example, one obtains $H_4Fe(CN)_6$ and $H_3Fe(CN)_6$. They are known respectively as hydroferrocyanic and hydroferricyanic acids, and give salts. The iron in these compounds does not respond to the tests which ordinarily show its presence.

Potassium Ferrocyanide, yellow prussiate of potash, $K_4Fe(CN)_6$, is obtained by heating together nitrogenous organic matter, like blood, horn, and so forth, with potassium hydroxide or carbonate in the presence of iron. The mass is leached, as the ferrocyanide is soluble in four parts of water. When the liquid is evaporated, large yellow crystals form. When brought in contact with ferric chloride, Prussian blue, an important pigment, is formed:—

$$3\,K_4Fe(CN)_6 + 4\,FeCl_3 = \downarrow Fe'''_4Fe''_3(CN)_{18} + 12\,KCl.$$

It will be noted that the iron is written in an unusual way. That is due to the fact that Fe_4 may be replaced as in any ordinary compound of iron, whereas the Fe_3 exists in the masked condition referred to above. The former is trivalent and the latter divalent.

Potassium Ferricyanide, red prussiate of potash, $K_3Fe(CN)_6$, is formed from the ferrocyanide by oxidation, usually by means of chlorine. It is very soluble in water. On bringing ferricyanide and ferrous salts together in solution, a precipitate known as Turnbull's blue is formed:—

$$2\,K_3Fe(CN)_6 + 3\,FeSO_4 = 3\,K_2SO_4 + \downarrow Fe''_3Fe'''_2(CN)_{12}.$$

In this case Fe_3 is replaceable and divalent, while Fe_2 is masked and trivalent.

EXERCISES

1. Calculate the specific gravity of cyanogen.

2. How many pounds of pure calcium cyanamide would be required to produce 40 pounds of ammonia?

CHAPTER LII

ALLOYS

We have considered the compounds of metals with non-metals and compounds of non-metals with non-metals. We may now study the compounds, quasi-compounds, or mixtures, among the metals. These homogeneous substances are called alloys. Some of them were undoubtedly known a long time before some of the metals were obtained in anything like a pure condition. For example, brass, an alloy of zinc and copper, was known before zinc. However, it is only within the last quarter of a century that alloys have been studied systematically, and even now they are not thoroughly understood. What has become known is based upon the application of principles of recent enunciation, the *Phase Rule*, first laid down by Willard Gibbs in 1874. This important generalization, which is used by the most progressive investigators in physical chemistry, is too complicated for explanation in an elementary text. Some of the simplest difficulties encountered, however, will be hinted at.

Copper and zinc are soft metals and have characteristic colors. When alloyed, they form brass, which is hard in comparison and has a color which is not intermediate between the two. Copper alloyed with antimony (Cu_2Sb) has a violet color (" Regulus of Venus "). Lead melts at + 327°, tin at + 232°, and bismuth at + 270°. An alloy of the three in the proportion 1 : 1 : 2 does not melt at the average temperature + 275°, but melts at + 95°. If the electric conductivity of silver is placed at 100, then the conductivity of gold is 80 by the same standard. The conductivity of an alloy of the two is not the average 90, but 15. The specific gravity of lead is 11.4 and tin 7.3. An alloy with 40 per cent. of tin has a specific gravity of 9.5. The calculated value for the mixture is 8.9. Platinum is insoluble in hydrochloric acid, but when present in some alloys it is soluble. As a rule, alloys are harder, hence more elastic and sonorous, than the constituent metals. The melting point is lower, the conductivity less, the specific gravity greater, and the chemical conduct different, which facts indicate that alloys are not mixtures, but chemical compounds. But chemical compounds require that the elements entering in them be in atomic ratio. This is not the case, for we may secure alloys of two metals in many different proportions. There are cases, however, where we may obtain definite crystalline compounds in which the metals are in strict atomic proportions, as for example, $SnMg_2$, $SbCu_2$, $SbCu_3$, and $SnCu_3$. These substances are distinct bodies, characterized by properties quite distinct from the constituents of which they are composed. In other cases there is an indication of the formation of compounds, but they are comparatively unstable and have not been isolated in a pure state. In still other cases the metals form no compounds whatever with each other, but dissolve to different extents in one another. In some cases, metals show only the slightest indication of union with or solution in each other.

Alloys are usually made by melting a definite amount of the metal with the highest melting point, with precautions to prevent oxidation, and adding the proper amount of the second metal in small pieces a little at a time and stirring the mixture. The material becomes homogeneous; that is, one metal is dissolved in the other. When cooled the mass solidifies, freezes, and retains its homogeneity in a measure. We thus have a *solid solution.*

We have learned that "a solution is a chemically and physically homogeneous mixture, of which the composition, within certain limits, can undergo continuous variation; the limiting compositions within which the mixture remains homogeneous are the limits of existence of the solution." That is to say, water will dissolve from 0 to 26.4 per cent of its weight of sodium chloride at + 18°, but not more, and be a homogeneous liquid. In the same way, solid aluminum will hold in solution from 0 to 50 per cent of zinc at + 380°, but no more.

The freezing point of water is lowered when salt is dissolved in it and in the proportion added. So when the metal X is added to Y, the fusing point of Y is lowered and in proportion to the amount of X added. Also, when a little of Y is added to X, the fusing point of X is lowered in the same manner, the extent being dependent upon the amount of Y added. If fusing point curves are constructed for the two cases, there will be a point where they intersect. A fused mixture of the two metals in the proportions indicated at that point will solidify as a uniform mass, a solid solution, or eutectic.

Usually a liquid solvent dissolves more of a solid solute at a high temperature than it does at a lower one. When the solution is cooled, the excess of the solute separates out as a solid, ordinarily crystalline. This is true also of solutions of liquid mixtures in each other. If the fused mixture has the metals present in any other proportion than that constituting an eutectic, and is allowed to solidify, the excess of the solvent, which is the metal in larger proportion, will separate in the pure condition. If the metals unite to form compounds, such as referred to, then the matter involves a compound and its solubility in the pure metal in excess, or the reverse. When there are several metals, they may form compounds among themselves, and each has a different solubility. As we cool the liquid, we have some of each metal or compound separating, as when we cool a water solution of mixed salts. The size of the crystals of each in the latter case depends in a measure upon the rate of cooling. This is also true for alloys, but the alloy is usually completely solidified, consequently we have a mixture, that is, a solid solution of metals and alloys in the metal. If a solidified alloy is polished and etched, the microscope will reveal the presence of the metallic compounds, the eutectic, and the pure metal in excess. The properties of the alloy are very dependent upon the rate of chilling.

A number of alloys has been prepared. Many of them are of tremendous commercial importance. Only a few of the various groups will be mentioned here, as attention was directed to others when the individual metals were considered.

Group I. An alloy of sodium with 10 to 30 per cent of potassium melts at zero, and remains liquid through a wide range of temperatures. It has been used for filling thermometers.

Copper forms a number of alloys. Brass is an alloy of copper and zinc, to which tin and lead are often added. Brass is hard, may be cast, and is easily worked with tools. Copper and tin form alloys known as bronze, gun metal (of which cannon were formerly made), and bell metal (with about 22 per cent of tin). With 33 per cent of tin, speculum metal is produced. It takes a high polish and is used in optical instruments. Copper, tin, and a small amount of manganese give manganese bronze, of which propellers for ocean steamships are made. It is strong and is little affected by salt water. Phosphor-bronze contains phosphorus instead of manganese. It is quite strong.

The "nickel" coin of the United States contains 75 per cent of copper and 25 per cent of nickel. German silver contains 60 per cent of copper, 20 per cent of zinc, and 20 per cent of nickel.

Copper with less than 10 per cent of aluminum gives an alloy possessing considerable strength and resembling gold in color.

Silver and gold are alloyed together, or more usually with copper, for useful purposes. The silver coins of the United States contain 10 per cent copper and are known as 900 fine, 1000 being pure silver. Gold coins contain 90 per cent gold, the remainder being copper or silver or both. Gold used for jewelry contains a larger proportion of copper or silver. Usually jewelry is made of from 12 to 16 carat gold. The difference in color noted in gold coins and jewelry is due to the different proportions of gold, silver, and copper.

Group II. Mercury dissolves many of the metals at ordinary temperatures. These alloys are called amalgams. Crystalline compounds may be separated in many cases. When sodium is placed in mercury, it dissolves with the production of much heat. On cooling, after sufficient sodium has been added, the sodium amalgam solidifies. Reference has already been made to it as well as to ammonium, silver, and gold amalgams. Tin amalgams were once used for "silvering" mirrors. Silver and tin amalgams, when first prepared, are soft, but quickly harden, hence they are used in dentistry.

Group III. Aluminum and titanium form an alloy almost as light as the former metal and very strong.

Groups IV and V. Tin and lead in the proportion of 4 : 1 form pewter; and 1 : 1 to produce common solder. If the proportion of tin is greater, it is known as "fine solder"; whereas if the lead is in greater amount, it is "common solder." Lead alloys with arsenic and antimony have been referred to. "Fusible metals" are alloys of lead, tin, and bismuth, and often cadmium. "Wood's metal," containing 4 parts of bismuth, 2 of lead, 1 of tin, and 1 of cadmium, melts at + 60.5°. Cerium alloyed with 70 per cent iron gives off brilliant sparks when scratched with a piece of steel.

Groups VI, VII, and VIII. Alloys of the metals in these groups are of immense commercial importance. Chrome, molybdenum, tungsten (and vanadium), and manganese steels have recently acquired noteworthy prominence, as mentioned. Ordinary iron and steel contain carbides and silicides, which form solid solutions with pure iron.

The platinum metals usually occur alloyed together in nature. Platinum-iridium alloys are harder and more resistant to the action of chemicals than either metal alone. The international metrical standards are made of platinum with 10 per cent iridium.

INDEX

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